Sandwell Beak Research Group
Energy and Environmental Science

Toronto Montreal St.John's
Vancouver Calgary Saskatoon

6870 Goreway Drive
Mississauga Ontario Canada
L4V 1L9
Telephone (416) 671-2606
Telex 06-983527

SBRG

REQ. NO. 1-9031

STUDY RELATING TO THE PRODUCTION OF OIL FROM LOW RANK CANADIAN COALS BY CONTINUOUS LIQUEFACTION - PHASES II AND III

FINAL REPORT

CONFIDENTIAL

BY

SANDWELL BEAK RESEARCH GROUP

WORK ON THIS PROJECT WAS CONDUCTED UNDER THE AUSPICES OF THE CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY, ENERGY, MINES AND RESOURCES, CANADA.

DSS CONTRACT SERIAL NUMBERS: OSQ81-00022/24
CANMET PROJECT NUMBER : 430602
CANMET SCIENTIFIC AUTHORITY: Dr. J.F. Kelly

26 Oct 1983

Sandwell Beak Research Group
Energy and Environmental Science

Toronto · Montreal · St John's
Vancouver · Calgary · Saskatoon

6870 Goreway Drive
Mississauga / Ontario / Canada
L4V 1L9
Telephone (416) 671-2606
Telex 06-983527

SBRG

23 October 1983

Dr. J. Kelly, Ph.D.
CANMET
Energy Research Laboratories
Energy Mines and Resources Canada
555 Booth Street
Ottawa, Ontario
K1A 0G1

Dear Jim:

We are pleased to submit to you the original and four (4) copies of the final report on The Study of Production of Oil from Low Rank Canadian Coals by Continuous Liquefaction, Phase II and III. The report contains a complete summary of work and results obtained during the period covered. We include in it your comments on the draft report, which we also enclose at your request.

We hope this satisfies your requirements. Upon your acceptance of this report, DSS will proceed with outstanding payments to us.

Yours very truly

SANDWELL BEAK RESEARCH GROUP

Gabriela Teodosiu

Gabriela Teodosiu
Manager, Coal Research Program

GT:jd
Encl.

PREFACE

This report presents the results of the third year of Stage 2 of the Canadian Coal Liquefaction Development Project. The project was conducted during the period April 1981-April 1982 by the Sandwell Beak Research Group and was funded by Energy Mines and Resources Canada and Sandwell and Company Limited. During the prior two years, one of Canada's first continuous direct coal liquefaction process development units (PDU) was designed, assembled and commissioned. During the period covered by this report, the PDU was operated for over 500 hours liquefying low rank Canadian coals. The main activities and achievements reported herein include:

1) Liquefaction of Saskatchewan lignite (Estevan) and Alberta Sub-bituminous (Roselyn) coals
2) A total of 15 experiments comprising both once-through and solvent recycle modes of operation
3) During the year the once-through testing program was completed and the work progressed to recycle operations with process-derived solvent recycle
4) The experimental program was conducted within a range of variables which include:

Reactor Temperature	425-440°C
Reactor Pressure	17.9-24.8 MPa
Feed Rate	3.6-7.8 kg/h

5) Approximately 400 L of coal-derived liquids were produced and used in product characterization studies, solids separation research, batch testing studies, coal liquids upgrading studies and as solvent in studies conducted by others in which EMR is a participant.
6) A study of solid separation techniques was conducted and three means of solids removal were used in the test program which incorporated process-derived recycle solvents.

TABLE OF CONTENTS

		Page
	PREFACE	
1.0	INTRODUCTION	1
2.0	SUMMARY/SOMMAIRE	3
	2.1 PDU Operation/L'Operation de l'Instalation Pilote	3
	2.2 Liquefaction Results/Resultats	4
	2.2.1 Once-Through/L'Operation Sans Recyclage du Solvent	4
	2.2.2 Coal-Derived Solvent Operation/Opérations Avec le Recyclage du Solvent	5
	2.3 Solids Separation/La Separation des Matieres Solides	9
3.0	UNIT DESCRIPTION	10
	3.1 Description of the Unit	10
	3.2 Description of the Unit Modules	14
	3.3 Data Acquisition	19
4.0	ANALYTICAL PROCEDURES	21
	4.1 Sampling Techniques	21
	4.2 Methods of Analysis	21
	4.2.1 Determination of Water Content	21
	4.2.2 Determination of Oils, Asphaltenes and Preasphaltenes	21
	4.2.3 THF Insolubles by Filtration	22
	4.2.4 Infrared Spectrometry	22
	4.2.5 Vacuum Distillation	22
5.0	OPERATION AND RESULTS	23
	5.1 Summary of Operations	23
	5.1.1 Objectives	23
	5.1.2 Once-Through Experiments	23
	5.1.3 Solvent Recovery and Recycle Runs	31
	5.2 Definitions and Data Handling	33
	5.2.1 Data Requirements	34
	5.2.2 Material Balance Calculations	34
	5.2.3 Definition of Conversion and Yields	36
	5.3 Feedstock Characterization	38
	5.4 Discussion of Once-Through Results	39
	5.5 Discussion of Recycle Runs	48
	5.5.1 Recycle Recovery by Vacuum Filtration	53
	5.5.2 Recycle Recovery by Vacuum Distillation	55
	5.5.3 Recycle Recovery by Centrifugation	64
	5.5.4 Solvent Recycle Runs - Conclusions and Recommendations	79

TABLE OF CONTENTS (Continued)

		Page
6.0	EQUIPMENT PERFORMANCE	84
	6.1 Slurry Preparation and Feed Module	84
	6.2 Fresh Gas and Gas Feed Module	85
	6.3 Reactor Module	87
	6.4 Valves	88
	6.5 Vacuum Distillation	89
7.0	REFERENCES	95

APPENDICES

I	Run Histories	96
II	Development of a PDU System for the Separation of Solids From Coal Derived Liquefaction Product	123
III	Batch Testing Conducted on the Cascade Reactor	136

LIST OF TABLES

Table		Page
3.1	Data Acquisition Schedule	16
5.1A	Summary of Operations	24
5.1B	Reactor Conditions for Once-Through Runs	25
5.2	Experimental Conditions for Once-Through Experiments- Lignite	26
5.3	Experimental Conditions for Once-Through Experiments -Sub-bituminous coal	27
5.4	Ultimate and Proximate Analysis of Coals	40
5.5	Petrographic Analysis of Coals	41
5.6	Analysis of Solvents	42
5.7	Once-Through Experiments - Summary of Results	44
5.8	Once-Through Experiments - Elemental Analysis of Results	49
5.9	Run No. 8 Results (Solids Removed by Filtration)	54
5.10	Solids Free Liquid Composition of Heavy Reactor Products-Run 8	59
5.11	Run No. 10. Results (Solids Removed by Distillation) Results	61
5.12	Solid Free Liquid Composition of Total Liquid Reactor Product - Run 10	67
5.13	Elemental Analysis of the Heavy Product During Recycle Run 10	68
5.14	Recycle Run No. 11 - Centrifuge Operation	70
5.15	Recycle Run No. 11 - Centrifuge Performance	71
5.16	Run No. 11 - Results (Solids Removed by Centrifugation)	72
5.17	Run No. 11 - Evolution of Solids Free M3X1 and Feed Composition (% wt.)	78
5.18	Comparison of Reactor Liquid Feed Composition as a Function of Number of Passes for the Three Recycle Runs	80
5.19	Comparison of Reactor Product Composition as a function of Number of Passes for the Three Recycle Runs	81
5.20	Operating Conditions and Results Obtained in Hydrocracking Lignite Derived Liquids	82
5.21	Quality of Oils During Hydrocracking of Lignite Derived Liquids Recycle Solvent	83

LIST OF FIGURES

Fig #		Page
3.1	Continuous Unit Flow Diagram	11
3.2	Continuous Unit Data Acquisition	18
5.1	Moisture Loss in slurry with stirring and Recirculation at 75 degrees C	29
5.2	Continuous Unit Recycle Mode Data Analysis	37
5.3	Conversion Once-Through Tests	45
5.4	Liquid Yields Once-Through Tests	46
5.5	Evolution of Conversion, Liquid Yield and Gas Yield with number of passes Recycle solvent via vacuum filtration	56
5.6	Evolution of Oxygen removal data with the number of passes. Recycle solvent recovered via vacuum filtration	57
5.7	Evolution of Heavy Product Composition as a function of time, Run 8	58
5.8	Evolution of conversion, liquid yield and gas yield with the number of passes. Recycle solvent recovery via vacuum	62
5.9	Evolution of Oxygen removal data with the number of passes Recycle solvent recovery via vacuum distillation	63
5.10	Run 10: Product Yields	65
5.11	Evolution of Heavy Product Composition as a function of time, Run 10	66
5.12	Evolution of conversion, liquid yield and gas yield with the number of passes. Recycle Solvent recovered via centrifugation	73
5.13	Evolution of Oxygen removal data with the number of passes Recycle solvent recovered via centrifugation	74
5.14	Evolution of Heavy Product Composition as a function of time, Run 11	75
5.15	Product Yields Run No. 11	76
5.16	Centrifuge Operation Run No. 11	77

CONTRIBUTIONS TO THE WORK

SBRG gratefully acknowledges the contributions to the work described in this report made by the following organizations and people.

Government of Canada

Scientific Authority	J.F. Kelly, EMR, Canmet
Contract Manager	E.K. Fresque, DSS

Project Manager and Primary Contractor

Sandwell Beak Research Group
Mississauga, Ontario

Project Technical Staff	G. Teodosiu, Program Manager
	E. Chornet, Research Director
	R. Arsenault, PDU Operations
	P. Groeneweg, Solid Separation Studies
	A. Vavlitis, Batch Studies
Analytical	S. L. Hodd, Executive Director
	R. Lega
	N. Lichacz
	T. Perdok
Operation and Support Staff	L. Howarth
	A. Poell
	G. Reitze
	D. Schneider
	M. Faulkner

Subcontractors

Special Consultant	Dr. C.A. Johnson, Princeton, N.J.
Solvent Characteristics	Dr. C. Roy, University of Sherbrooke
Elemental Analysis	S. Jenkins, Beak Consultants Limited

1.0 INTRODUCTION

In 1979, Energy Mines and Resources Canada (EMR) and Sandwell and Company Limited (Sandwell) jointly began the second stage of a program to research the potential for liquefaction of low-rank coals as a source of liquid fuels. The work was managed and conducted by the Sandwell Beak Research Group (SBRG), the energy research and development division of Sandwell.

This second stage of the program followed two years of study conducted by SBRG for EMR examining the fundamentals of direct liquefaction as they could apply to Canadian lignite. The results of these studies are contained in two reports, "Liquefaction of Low Rank Coals - Phase I", May 1978 and - Phase II, April 1980, which describe the Stage I fundamental research studies.

These reports concluded that lignite liquefaction is a technically feasible process based on the results of a review of the literature, fundamental equilibrium thermodynamics and a batch hydrogenolysis experimental program using Estevan lignite. The highest conversions and liquid oil yields obtained experimentally were 85.3% and 63.4% respectively on an MAF basis.

As a result of these encouraging findings, EMR and Sandwell jointly began a Stage II program to advance the original work program.

Although the research program based on batch experiments gave useful information, continuous processing equipment was considered to be essential for meaningful process development work and simulation of actual liquefaction conditions on a commercial scale. Thus the objective of the first phase of the Stage II study was to construct a continuous direct liquefaction process development unit (PDU). A PDU with a nominal 10 kg/h slurry feed rate and both gas and solvent recycle was designed. It was installed in the energy research facilities of SBRG in Mississauga, Ontario and became operational in February, 1981. The first phase report entitled "Production of Oil from Canadian Low Rank Coals by Continuous Liquefaction 1981" describes the PDU in detail.

This report is a summary of Phase 2 and 3, Stage II, the first full year of coal liquefaction research and process development using the PDU.

The objectives of this one year program were as follows:

1) To extend the knowledge on the liquefaction properties of two Canadian low rank coals through experimentation in a continuous mode in the PDU using both a once-through and recycle mode of operation,
2) to evaluate the influence on conversion and liquid yield of such conditions as temperature, pressure, reaction time, recycle oil fraction and gas mixture composition, and
3) the development of preliminary economics of a process for direct liquefaction based on the results of the experimental program and a plan for the demonstration at a larger scale.

The program was amended during the year to include an in-depth study of the problem of solids separation, which is the single most critical problem affecting the economic viability of liquefaction of low rank coals. As a result of this effort, Sandwell has filed for a patent for a novel process which should significantly improve the yield of net liquid products. Further development and demonstration of this process is required before valid economic studies or scale-up projects can be undertaken.

A total of 14 experiments were conducted in the once-through mode of operation. Anthracene oil was employed as a solvent in most cases, except two experiments which used a partially lignite-derived solvent and a hydrogenated coal-derived solvent obtained from the Wilsonville, SRC-1 pilot plant. Experiments were conducted using Estevan lignite (10) and Roselyne sub-bituminous coal (4). Except for one experiment, hydrogen gas was used as the reducing gas.

Three recycle experiments were conducted using filtration, vacuum distillation and centrifugation as the means of solvent fractionation. All recycle runs were conducted on the same coal under identical operating conditions.

A separate study on solids separation was undertaken to develop a PDU system for the separation of solids from coal derived liquefaction product. This report discussed the results of a literature review on this subject and bench-scale testing of several of the alternatives. Work is continuing leading to the demonstration of a new process for solids separation and product recovery.

A number of equipment improvements, design changes and additions were completed during the year to make the unit safe, reliable and efficient to operate. These improvements as well as run histories and equipment performance are described in this report.

2.0 SUMMARY

The direct liquefaction of coal promises to be an efficient and economic process for the production of liquid fuels. In Canada, large resources of reasonably priced low rank coals could supply the necessary feedstocks to a synfuels industry. To realize the potential of those resources, it is necessary to develop a technology which can efficiently transform these coals into quality liquid fuels.

The two previous years work in this program, dedicated to developing a technology for these coals, had resulted in the completion of a 10 kg/h continuous liquefaction process development unit which is an essential tool for advanced process development. With this new facility, an ambitious research program was undertaken on Canadian lignite and sub-bituminous coals. The following describes the results of the study in terms of the operation of the PDU, research on the primary liquefaction stage of the process and a special investigation on solid separation.

SOMMAIRE

La liquéfaction directe du charbon promet d'être un procédé économique et efficace pour la production des combustibles liquides. Le Canada a des grandes quantitiés de charbons pauvres (lignites et sous-bitumineaux) a un prix raisonable qui peuvent fournir les matiéres premiéres pour une industrie de combustibles liquides. Afin d'exploiter ce potentiel il faut développer une technologie qui pourra transformer de façon efficace ces charbons en combustibles liquides de bonne qualité.

Les deux années précédentes de ce programme visant le développement d'une technologie pour la valorisation des charbons pauvre ont eu comme résultat la construction d'une installation pilote de 10 Kg par heure, ce qui est un outil essentiel au développement poussé d'un tel procédé. G.R.S.B. s'est engagé dans un programme de recherche tres ambitieux utilisant cette unité pour la liquéfaction des lignites et des charbons sous-bitumineux de l'ouest du Canada. Ce rapport présente les resultats de la deuxiéme et troisième étape de cette étude en ce qui concerne l'opération de l'unité pilote, des recherches sur la premiére étape du processus de la liquéfaction et une investigation spéciale sur la séparation de matières solides dans la produit.

2.1 PDU OPERATION

During the first full year of operation of the PDU, the unit operated for more than 500 hours and generally performed very well. Numerous improvements were made throughout the year to improve reliability, safety, sampling, flow measurement and control, operational range and efficiency of

L'OPERATION DE L'INSTALATION PILOTE

Durant la premiére année de l'opération du pilote l'unité fonctionna pendant plus de 500 heures et la performance fut tres satisfaisante. De nombreuses modifications ont été portées à l'equipment pour augmenter le dégré de confidence, et la securité du travail et pour améliorer l'échantillonage et

operation. At the end of the year the unit was in excellent condition and operational in all respects. Further changes are proposed in order to fully integrate a continuous solids separation module in the process. Other modifications would provide additional backup and automation.

le contrôle de l'opération autant que l'efficacité des opérations et l'étendue des parametres d'opération. A la fin de l'année l'unité s'est presentée dans un excellent état d'opération. On propose pour l'année à venir d'ajouter de l'équipment afin de permetre l'intégration du procedé de séparation de matières solides du produit et la récupération du solvent de recyclage. Aussi on envisage l'addition d'instrumentation et équipement de réserve et l'automatisation de l'unité.

2.2 LIQUEFACTION RESULTS

RESULTATS

The PDU was operated initially in a once-through mode of operation and later with solvent recycle with multiple passes. Both types of operation produced new knowledge on the process.

Au début l'unité fut opérée sans recyclage du solvent et puis avec recyclage du solvent par passes multiples. Le deux modes d'opération ont géneré des résultats intéressants et ont permis d'avancer les connaisances sur le processus.

2.2.1 Once-through Operation

L'operation Sans Recyclage du Solvent

In once-through operation, an extraneous solvent was used to prepare the coal slurry. None of the product was recycled . The significant findings of this part of the program are as follows.

Dans l'opération sans recyclage du solvent, le charbon fut suspendu dans un solvent procuré au début de l'essai. Aucun produit fut recyclé. Les conclusions significatives de cette partie du program sont les suivantes.

Repeatability

Reproduction

A total of eight (8) tests were conducted on Estevan lignite, four (4) of which were under conditions that were sufficiently similar to evaluate the repeatability of the experimental procedure. An analysis of these tests revealed that the results were reproducible, particularly for total conversion and liquid yield.

Le lignite d'Estevan fut utilisé dans huit (8) essais, les conditions dans quatre (4) des ces essais furent assez similaires pour permettre l'évaluation de la reproduction des procédures experimentales et des resultats obtenus. L'analyse de ces essais indigue que la conversion et le rendement en liquide étaient reproductible.

Accordingly the program moved into a recycle operation mode, which must be considered a prerequisite to further optimization of the primary liquefaction step of the process.

résultats sont trés dépendents de la qualité du solvent utilisé et que seulement des essais effectués avec recyclage du solvent, en régime de stabilité (steady state) peuvent constituer une base pour le développement d'un procédé.

La phase suivante du program de recherche de GRSB a compris des éssais effectués avec récyclage du solvent, comme un prémier pas vers l'optimisation de l'étape initiale de la liquéfaction.

2.2.2 Coal-Derived Recycle Solvent Operation

The solvent available for recycle depends on the solid-liquid separation system used and in turn the liquefaction and hydrogenation process is dependent on the properties of the solvent. Since the operation and performance of these two unit operations are mutually dependent, the overall process can only be optimized when integrated. The change of any process parameter in either the reaction or solids separation steps must be viewed in the context of the entire process.

Three experimental runs were were conducted with recycle of the product as solvent. In each of the runs a different method of solvent recovery was employed. This provided an opportunity to assess not only the performance of the separation procedure but also the effect of the resultant solvent quality on the primary liquefaction stage.

In the most successful run the recycle solvent was a mixture of 250-450°C vacuum distillation cut and non-distilled as received

Opérations Avec le Recyclage du Solvent

La fraction du produit qui peut être utilisée comme solvent pour recyclage, dépend du système de séparation des solides, et à son tour le processus de liquéfaction et d'hydrogénation dépend des propriétés du solvent. Parce que l'opération de ces deux étapes est interdépéndente il faut les intégrer pour arriver à une optimisation du processus de liquéfaction dans le sens que chaque modification porteé aux paramêtres de réaction, ou de la séparation de solides, va avoir des conséquences sur la performance des deux étapes.

Durant la Phase III de ce program, trois essais avec recyclage du solvent furent effectués. Pour chaque essai une methode différente de récupération du solvent fut utilisée, ce qui a permis de juger la performance de chaque procédure de séparation et aussi l'effet que la qualité du solvent obtenu par chaque procédure a eut sur l'étape de liquéfaction.

Les meilleures résultats furent obtenus avec un solvent de recyclage qui était un mélange de produit lourd comme tel et d'une fraction recupereè par la distillation sous vide.

slurry product. Thus a portion of solids was returned. Stable operation was achieved after four passes. Compared to once-through operation under similar conditions the conversion increased from 84.1% to 95.3% maf of fresh coal. Similarly, liquid yields increased from 61.4% to 68.4% This corresponds to gross yields of 4.4 bbl/tonne maf coal. These are excellent results, as good as those obtained by any other process on lignitic coals.

In the other recycle runs, employing vacuum filtration and centrifugation for solids separation, stable operation was not achieved. The use of these procedures alone did not allow for the necessary removal and control of the preasphaltenes and asphaltenes in the recycle solvents. Rather these components caused an increase in the viscosity and gravity of the slurry product until the physical separation processes were no longer effective. These runs revealed the importance of maintaning the appropriate ratio of preasphaltene and asphaltene compounds relative to oils (cyclohexane soluble material) in the recycle streams. This can be achieved only by the removal of these non-distillable fractions from the process at a rate sufficient to prevent accumulation in the process.

The recycle runs clearly indicate that conversions greater than 90% can be achieved and that excellent liquid yields can be obtained although the products need further upgrading.

De cette façon une portion des solides sortis du réacteur était retournée à la réaction. Un régime d'opération assez stable fut atteint aprés quatre passes. La conversion du charbon obtenue dans cet essai était 95.3% "m.a.f.". Ce qui represente une augmentation pour raport au resultat de 84.1% obtenu dans des conditions similaires mais sans recyclage du solvent. Dans la même direction, le rendement en liquide obtenu avec recyclage du solvent etait supérieur à celui obtenu sans recyclage (68.4% comparé a 61.4%). Ces résultats correspondent à un rendement brute de 4.4 barils per tonne de charbon sec sans cendres (m.a.f.). Ces résultats sont excellents, et ils sont en ligne avec des résultats obtenus par des autres procedés appliqués aux lignites.

Dans les deux essais utilisant la filtration sous vide ou la centrifugation comme méthodes de séparation des matières solides un régime stable d'opération ne fut pas atteint. Aucune des ces deux méthodes utilisées par elle même a produit le dégré nécessaire d'enlevement des solides et des composés asphaltiques dans le solvent de recyclage. Par contre, ces composés ont causé par leur accumulation une augmentation de la viscosité et de la densité du produit lourd, qui a eu comme conséquence la perte d'efficacité du procedé physique de séparation. Les résultats de ces deux essais on révélé l'importance du contrôle du niveau des produits asphaltiques dans le solvent de recyclage. Ce contrôle est réalisable seulement si les produits asphaltiques sont enlevés du systéme dans la même mesure qu'ils sont formés dans la réaction.

Les essais avec le recyclage du

Temperature

The temperatures used throughout were within a narrow range (425-440 degrees C) and no discernable trends with temperature were noted.

Operating Conditions

Based on the results of the once-through tests, it was decided that reasonable performance and yields could be obtained with a temperature of 440°C, pressure of 24.2 MPa and liquid hourly space velocities not greater than 1.0. These conditions were selected for the recycle operations.

Solvent Types

For most of the experiments an anthracene oil was used as a solvent. Tests were also conducted with a distilled fraction of once-through lignite derived product and with Wilsonville hydrogenated solvent. The conversions obtained were similar to those produced with Anthracene oil. Liquid yields varied greatly however, with the partially lignite derived solvent increasing the total liquid yield, albeit of generally lower quality. The tests with Wilsonville hydrogenated coal-derived solvent resulted in a reduction of liquid yield. The dependency of the once-through operation on recycle solvent quality is such that only work based on actual recycle of coal derived solvents at steady-state can be used for process development purposes with any validity.

similaires, les essais utilisant le lignite et sous-bitumineux ont donné résultats comparables.

Température de réaction

Les niveaux des témperatures se sont situés dans les limites assez étroites de 425°C, a 440°C et il n'y a pas en de différences remarquables dans les résultats.

Conditions d'Operation

Les resultats obtenus dans les essais sans recyclage du solvent indiquérent que les meilleures performances correspondent à une temperature de 440°C une pression de 24.2 MPa et une vitesse spatiale horaire du liquide de moins de 1.0. Ces conditions d'operation ont été choisies pour les essais avec recyclage du solvent.

Type de solvent

L'huile d'anthracene fut utilisée comme solvent pour la plupart des essais. Deux essais furent effectués avec une fraction distillée du produit obtenu en préalable par GRSB à partir du lignite et aussi deux autres essais furent effectués avec une fraction distilleé du produit hydrogéné provenant de l'installation SRC de Wilsonville en Alabama. Des conversions du charbon similaires furent obtenus avec tout ces solvents. En ce qui concerne le rendement en liquides il y a eu des différences remarquables. L'utilisation du produit qui était partiellement derivé du lignite a donné des rendements en produit liquide supérieures à ceux utilisant l'huile d'anthracéne. Quant aux essais avec le solvent de Wilsonville les rendements en produits liquides furent nettement inférieurs à ceux obtenus avec l'huile d'anthracene. Ceci démontre que les

Residence Time

The period of exposure of the coal slurry to the reaction conditions was found to influence the conversions. Conversions above 80% were invariably achieved for a LHSV below 1.0 (corresponding to liquid residence time of greater than one hour) and pressures above 24.2 MPa. The kinetics are thus very important in the primary liquefaction stage.

Le temps de residence dans le reacteur

Les resultats ont demontré que la conversion du charbon fut beaucoup influencée par le temps moyen que le charbon avait subit les conditions de température et pression en presence de l'hydrogéne dans le reacteur. Un niveau de conversion de 80% fut toujours atteint pour une vitesse spatiale horaire du liquide (LHSV) de moins de 1.0 (ce qui correspond a un temps moyen de residence dans le reacteur de plus d'une heure) quand l'hydrogéne seul était utilisé comme gaz d'alimentation. Ceci indique que la cinétique de réaction est un facteur primordial.

Reducing Gas Mixtures

Only one experiment was conducted with a gas mixture of CO and H_2. It was expected that larger conversions would be produced with syngas, however conversions of only 76.4% were obtained. The liquid yield was higher than a comparable test with hydrogen suggesting that further research on this option should be conducted.

Le mélange de gaz d'alimentation

Un seul essai utilisant un melange de H_2 et CO fut réalisé. L'effet du gaz de synthése ne s'est pas materialisé dans la direction comptée, la conversion obtenue étant 76.4% (inférieure au résultat attendu). Mais ce qui étant extremement encourageant est le rendement en liquides qui fut supérieure à celui obtenu avec l'hydrogéne pur. On éstime que les recherches utilisant un gaz de synthése doivent étre continueés.

Lignite vs Sub-bituminous Coals

Four (4) experiments were conducted with an Alberta sub-bituminous-C coal (Roslyne Mine). The conversions obtained with sub-bituminous coal appear to be lower than the lignite, however the range of test conditions was not sufficiently broad to cover the probable optimum. On closer inspection and comparison of the results with the lignite runs at similar LHSV rates the sub-bituminous coal gives comparable results to the lignite.

Comparaison des charbons: le lignite vis avis le charbon sous bitumineux

Quatre (4) essais furent effectués avec un charbon sous-bitumineux d'Alberta (celui de la mine Roselyne) Les conversions obtenus étaient inférieures à celles obtenues avec le lignite, mais on considére que l'étendue des conditions d'opération n'était pas suffisante pour déterminer les conditions optimales.

L'analyse des résultats montre que lorsque les vitesses spatiales horaires du liquide étaient

2.3 SOLIDS SEPARATION

The solids separation part of the direct liquefaction process is a critical step in the entire process. For low rank and/or high ash content coals this step becomes even more important. Without an effective separation process net yeilds of product can be significantly less than the reported gross yields. The separation step is important from the standpoint of product recovery, removal of solids from product streams and the recovery and program have resulted in some new separation process concepts, which are expected to optimize the product recovery, solids separation and solvent selectivity aspects of this unit operation. In the next stage of the program, these concepts will be developed and demonstrated.

solvent ont demontrés que des conversions supérieures à 90% peuvent être atteintes et que des excellents rendements en produits liquides sont possibles, mais la qualitée du produit liquide brute n'est pas satisfaisante et il doit être traité d'avantage.

LA SEPARATION DES MATIERES SOLIDES

L'étape de séparation des matiéres solides du produit est une étape critique dans le procédé de liquéfaction directe du charbon. Dans le cas des charbons pauvres ayant une haute tenure en cendres, cette étape devient encore plus importante. Sans un procedé efficace de séparation, les rendements nets en liquide seront beaucoup inférieurs au rendements bruts. Aussi l'étape de séparation est importante pour la récuperation du produit, l'élimination de matières solides et la sélectivité du solvent de recyclage. Le travail de recherche commencé dans ce programme a fourni des conceptes nouveaux pour le processus de séparation qui améliorent beaucoup la récupération du produit liquide, la sélection de la fraction de recyclage, et l'efficacité de l'élimination des solides. Ces conceptes serront développés d'avantage dans l'étape suivante du programme.

3.0 UNIT DESCRIPTION

3.1 DESCRIPTION OF THE UNIT

Figure 3.1 is a simplified flow chart of the continuous flow system as it stands at the completion of the present contract.

Coal Slurry Preparation

The preweighed and ground coal is slurried batchwise, under nitrogen atmosphere with the selected solvent in the slurry preparation vessel M2X1. A recirculation pump was added and the stirring profile was modified after the commissioning runs, in order to obtain a better and faster suspension of the coal in the solvent.

The coal content in the slurry is maintained in the range of 32 to 38% (wt, m.f.). The coal was not dried after grinding. The moisture content of the ground coal used varies slightly from around 21% for the lignite and 12% for the subbituminous C.

Periodically the batch of slurry is transfered into the slurry feeding vessel M2X2, which is equiped with heating and stirring. A high volume centrifugal recirculation pump provides additional mixing to avoid settling of the coal in the feeding vessel and in the feed lines, and also supplies the high pressure slurry pumps.

Two high pressure piston pumps are used alternately to feed the slurry. The Milton Roy pump was installed half way through the year in order to alleviate the slurry feed problems due to excessive check valve and seal packing failures encountered with the Bran and Lubbe pump.

Slurry Preheating

The coal slurry is preheated to a maximum of 300°C in a separate preheater before entering the upflow reactor.

A portion of the hydrogen rich feed gas can optionally be added to the coal slurry, upstream of the preheater inlet. The feed gas stream consists of either pure fresh hydrogen or recycle scrubbed gas plus sufficient fresh hydrogen to keep the overall gas composition above 90% hydrogen by volume.

Gas Feed and Preheating

Fresh hydrogen from the manifolds, or a mixture of fresh hydrogen and scrubbed recycle gas or a mixture of fresh hydrogen and carbon monoxide are supplied either into a storage tank (M6X1) or directly into the suction of a diaphragm

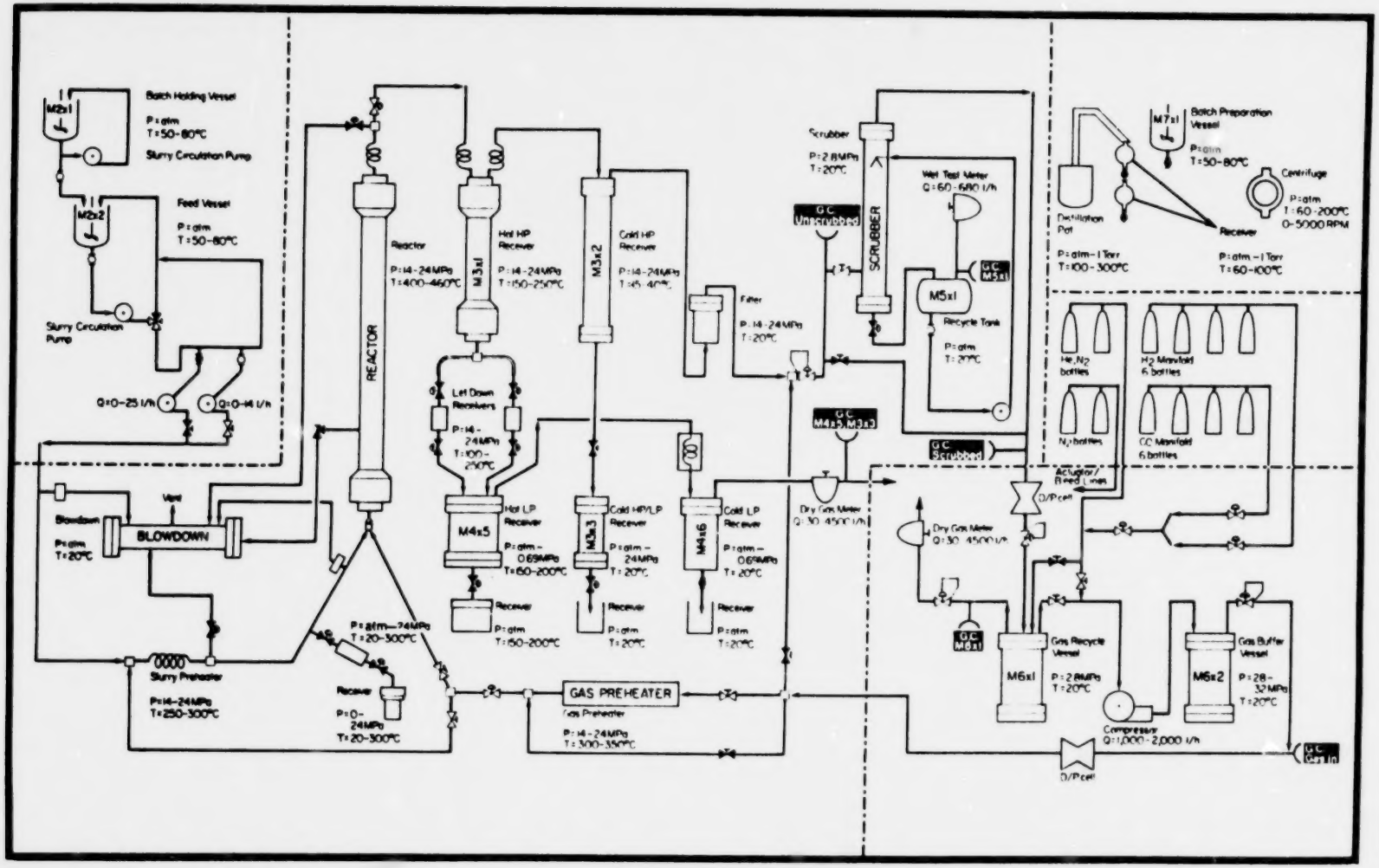


Figure 3.1 SBRG Continuous Unit Flow Diagram: Volumes and Typical Operating Conditions

compressor which boosts the gas pressure to about 32 MPa. The compressed gas is stored in a high pressure buffer tank (M6X2), out of which it is supplied through a pressure regulator into the unit. The flow of the total gas in, and recycled gas are measured with differential pressure gauges.

The gas stream into the system is preheated electrically to 350°C before it reaches the reactor. The system provides for supplying a portion of the hot gas into the slurry line and also for bypassing the preheater in case cold gas is required for reactor temperature quench.

Reaction Zone

The preheated coal-slurry and gas streams are fed into a mixing chamber situated below the upflow reactor. A well mixed three phase stream enters the base reactor and travels upflow through the reactor. The reactor is maintained at constant temperature (in the range 380°C to 460°C) by the use of four (individually controlled) electical heaters. The range of reactor pressure tested varied between 17.25 and 24.15 MPa. The slurry flow was such as to allow residence times in the reactor of 30-60 minutes.
The effluent of the reactor is cooled to around 250°C when it reaches the first separator.

High Pressure Gas and Slurry Separation

The vapor and slurry phases are separated in the High Pressure Separator (M3X1). The vapor phase from the separator containing water vapor, light products in the range of naphta's, gases produced (CO, CO_2, H_2O, CH_4 C_2's, C_3's) and unreacted hydrogen is cooled in a water cooled condenser to 20-25°C. During the experimental work the condenser was repeatedly plugged which required modification of the condenser to a water cooled jacket around the cold high pressure receiver M3X2. The uncondensed gas phase is vented to the scrubber through the back pressure regulator M3BPV.

The condensed light hydrocarbon and water collect in M3X2 and are evacuated periodically through receiver M3X3 using a manual pressure let-down procedure.
The liquid slurry from M3X1 is continuously evacuated through the pressure let-down valves and it is collected in the low pressure high temperature flash tank M4X5.

Routinely M4X5 is emptied every hour and the product is weighed and analysed for solids and water content. In the recycle runs this product is further processed for solids removal and is partially used as recycle solvent.

The vapor phase flashed out of M4X5 is condensed in a water cooled condenser and collected in the low pressure, low temperature receiver M4X6 which is emptied manually every hour. The product, containing most of the

water produced, is weighed and the organic phase is then separated and stored for further analysis.

Gas Recovery and Recirculation

The gas stream released from the back pressure regulator M3BPRV is scrubbed in a packed tower by contacting countercurrent in a solution of sodium hydroxide. The scrubber is maintained at a pressure around 2.8 MPa. The hydrogen sulphide and most of the carbon dioxide are removed and the scrubbed gas containing around 75% hydrogen, is either mixed with fresh hydrogen and recirculated into the system or vented after being measured and analysed chromatographically.

The other vent gases flashed out in M4X1, M4X5, are measured, analysed and vented into a bubbler filled with a solution of sodium hydroxide.

Vacuum Distillation Unit

The heavy oil fraction collected in M4X5 can be subjected to vacuum distillation in order to recover the solvent fraction.

The equipment used for vacuum distillation consists of a batch operated vacuum still and packed column, electrically heated and connected to a vacuum pump via liquid-nitrogen-cooled traps.

Solvent Recovery

The solvent fraction used for slurry preparation in the recycle runs was obtained by various means of solids removal.

In the past year three such methods were tested with various degrees of success:

- Vacuum distillation of a portion of the product using a batch operated vacuum distillation unit.
- Filtration of all or only a portion of the product evacuated from M4X5 using an improvised vacuum filter.
- Centrifugation of all or only a portion of the M4X5 product using an inhouse-modified continuous centrifuge.

The solvent was obtained by combining a fraction of solids-free or having a very low THF insoluble content product, with a portion of the M4X5 product directly out of the unit, in a heated, agitated vessel (M7X1). After sampling and THF insoluble determination, coal was added in order to obtain the desired solids concentration in the slurry feed.

3.2 DESCRIPTION OF THE UNIT MODULES

A modular concept was used in designing the system in order to facilitate the operation, maintenance and data acquisition. Mass balances can be calculated over each module and also changes can be made within each module without disturbing the others.

The system can be regarded as a combination of seven modules:

- slurry preparation and feed
- fresh gas manifolds
- reactor
- pressure let-down and product collection
- gas scrubbing
- gas recirculation
- solvent recovery

The gas feed-lines, storage and compressor are installed in a separate room from the rest of the system.

The Slurry Preparation and Feed Module is composed of a 50L slurry preparation tank provided with a multi-blade stirrer, electric heater and connection to inert gas and to the slurry feed tank. The loading of this tank is made batch-wise, each batch being enough for 8 hours unit operation at a feeding rate of 5 kg of slurry/hour. From this vessel, the slurry is transferred to the slurry feed tank. The construction of this tank is similar to that of the preparation tank but for the purpose of feed rate monitoring, this vessel is suspended on a load cell. The slurry is continuously recirculated by a low-pressure centrifugal pump at a sufficient rate to keep the coal in suspension. The slurry is heated under an inert gas blanket at all times. A high-pressure piston pump takes suction from the recirculation line at a pressure of 50-70 kPa. The slurry feed rate can be changed by adjusting the stroke.

Two such high pressure piston pumps are installed in parallel -

- Bran and Lubbe model No. N31
- Milton Roy Simplex model B (MR1-84-92)

The Fresh Gas Module includes a separate manifold for each of the following gases: hydrogen, carbon monoxide, nitrogen and helium; each provided with pressure regulators and flow meters. The hydrogen and carbon monoxide manifolds are made of 1/4" slim line 316 SS tubing. Each cylinder is connected by a brass coil to an arrangement of one check valve, one globe valve and a tee fitting to the manifold. There is one pressure gauge for each manifold and one pressure regulator to ensure constant feed pressure to the rotameters and the compressor. The hydrogen and carbon monoxide manifolds have 6 ports (3 cylinders in use, 3 full in wait) and the inert gas manifold has 3 ports.

The fresh gas is supplied from commercially available cylinders. The flow

of each individual gas is regulated by micrometric valves and the H_2/CO rate can be varied to obtain the desired concentration after combining with recycle gas.

The Reactor Module is comprised of the slurry preheater, the gas preheater, the upflow reactor, hot high-pressure receiver, the cold high-pressure receiver, the condenser and the backpressure regulator.

The slurry preheater is made of a coil 20 ft of high pressure, 316 SS tubing 3/8" imbedded in a heat transfer cement block, heated by an electric heater. The gas preheater is a 1" diameter pipe provided with strip heaters. Temperatures in both preheaters are measured and regulated from the temperature of the fluid leaving the preheater. The provision of introducing a split gas flow before and/or after the preheater is a built-in option serving a double purpose: to prevent slurry preheater coking in case of a temperature-run in the preheater and to help cool the in-flowing slurry in either the preheater or the reactor in case of a temperature run in the reactor.

The reactor is a 6 cm diameter 215 cm long 316 SS tubular upflow reactor, built with modified high-pressure Bridgeman closures and provided with four heating zones, individually controlled from thermocouples placed directly in the flow. The outside wall temperature is also monitored.

The high temperature, high-pressure receiver (M3X1) where the first flash takes place is a 7.5 cm diameter by 86 cm (316 SS) and it is provided with the same type of closures as the reactor. The liquid level is kept constant with the help of a gamma ray level indicator which controls the operation of pressure let-down valves.

The vapor phase is cooled to around 20°C in a water cooled jacketed receiver which is 8 cm diameter by 80 cm flanged vessel, (316 SS). All high pressure vessels have been designed to withstand a working pressure of 35 MPa at 450°C.

The liquid phase from the hot high-pressure receiver is evacuated via the pressure letdown module. The heavy product pressure let-down module is constitued of two separate trains, each comprising two sequentially operated Badger Meter Research valves, with Tungsten Carbide seats and stems, actuated on/off, with a 50 cm^3 intermediate vessel in between. The timing of the valves is manually adjusted, based on the indication of the gamma-ray indicator, the feeding rate and reaction parameters.

The slurry stream can be directed to either of the let-down trains while the other one is completely isolated allowing eventual repair work to proceed.

The heavy liquid stream off the let-down system is collected in a 15L, electrically heated hot receiver operating at max. 690 KPa where the last of the dissolved gas, water vapors and products boiling lower than 200°C are

TABLE 3.1: SBRG CONTINUOUS UNIT DATA ACQUISITION SCHEDULE

STREAM	COMPOSITION ANALYSIS	COMPOSITION FREQUENCY	FLOW METHODS OF MEASUREMENT	FLOW FREQUENCY
Feedstock				
coal	proximate ultimate metals % THF insolubles	as required	spring scale (± .05 kg)	each batch
starter solvent	elemental distillation % H_2O	as required	spring scale (± .05 kg)	each batch
recycle solvent	% THF insolubles % ash % H_2O	each batch	spring scale (± .05 kg)	each batch
gas in	% vol. H_2, CO CO_2, CH_4, C_2 C_3, H_2S	2 hours	D/P cell calibrate for each run (± 5%)	continuous
feed slurry	% THF insolubles % H_2O % ash	at least 3 times/batch as required	strain gauge (± .1 kg)	continuous manually recorded every 1/2 hour
Products				
heavy (M3X1)	% THF insolubles % H_2O	1 hour as required	not measured	
(M4X5)	% THF insolubles % ash % H_2O distillation elemental or distillation cuts solvent extraction	as required	spring scale (± .05 kg)	1 hour
light (M4X6)	% H_2O % organics distillation elemental or distillation cuts	as required	spring scale (± .05 kg)	1 to 3 hours
Solvents	% H_2O % THF insolubles % organics % ash distillation elemental % oils, asph. & preasph.			

TABLE 3.1: (continued) SBRG CONTINUOUS UNIT DATA ACQUISITION SCHEDULE

STREAM	SAMPLING		WEIGHING	
	ANALYSIS	FREQUENCY	TYPE	FREQUENCY
Residue	% THF insolubles % ash % oils % asphaltene % preasphaltene elemental	as required	Spring scale	as required
Light fraction	% H_2O % organics distillation elemental or distillation cuts	as required	spring scale ($\pm$ .05 kg)	1 to 3 hours
Gas to scrubber	GC analysis for H_2, CO, CO_2 C_1, C_2, C_3, H_2S	2 hours	not measure	
Scrubbed gas	GC analysis for H_2, CO, CO_2 C_1, C_2, C_3, H_2S	2 hours	D/P cell calibrated for each run	continuous (integrated
M3X3 and M4X5 off gases	GC analysis for H_2, CO, CO_2 C_1, C_2, C_3, H_2S	2 hours	dry gas meter	continuous (readings periodic)
M5X1	GC analysis for H_2, CO, CO_2 C_1, C_2, C_3, H_2S	2 hours	wet testmeter	continuous (readings

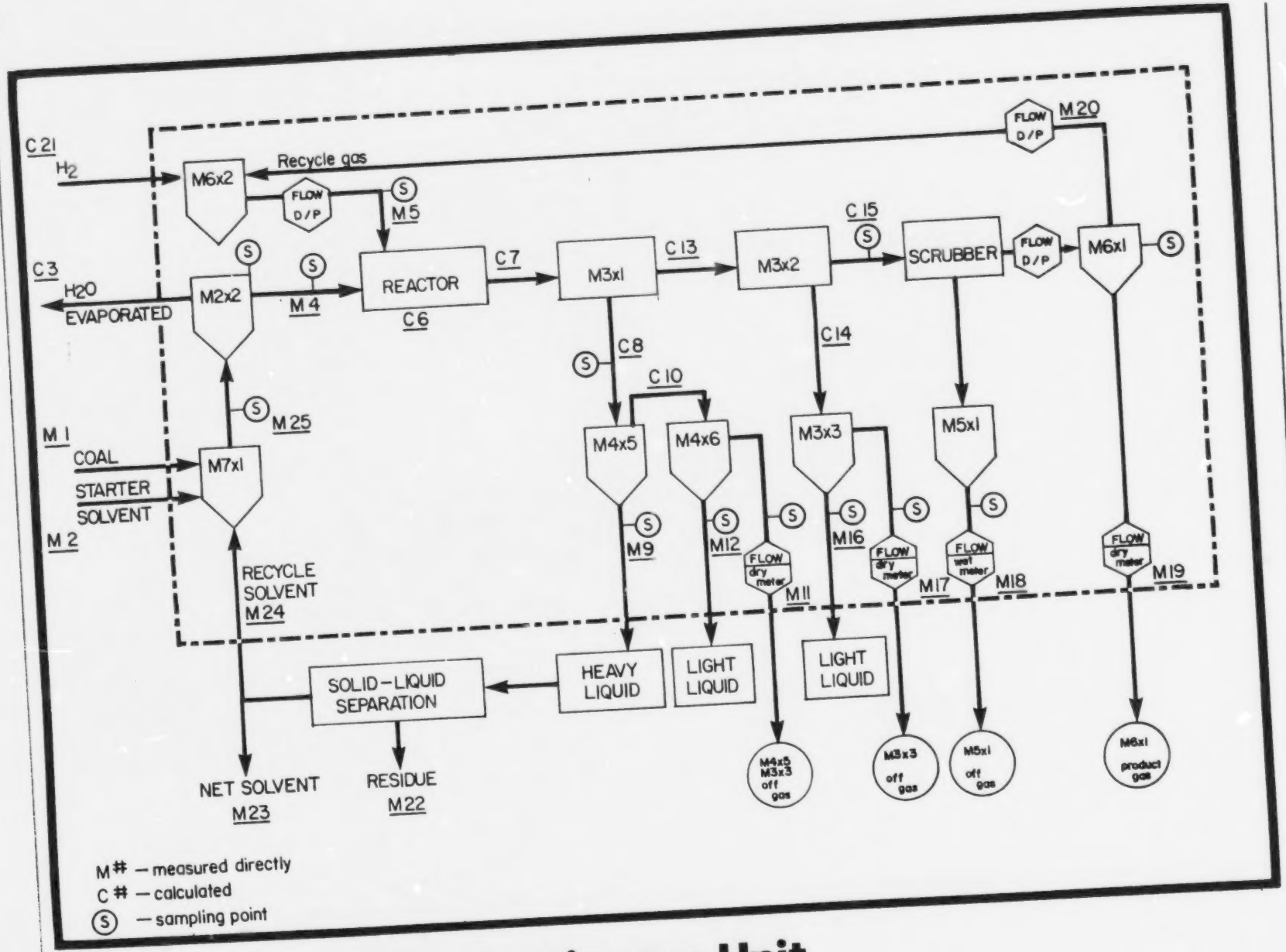


Figure 3.2 SBRG Continuous Unit Data Acquisition

leaving the liquid phase in the process of the pressure release, and condensed in a water cooled condenser to be collected as intermediate product.

The Gas Scrubbing Module operates at ambient temperature and 4 MPa. The scrubber itself is a 4" diameter, 210 cm packed column where the gas moves counter current to the absorbing medium which can be water, caustic solution or methanol. The absorbent solution is circulated with a pump to the top of the scrubber and its composition is periodically analysed. The solution leaving the scrubber through a bottom valve is kept in a closed tank connected to the exhaust system in order to allow the dissolved gases to escape.

The Gas Recycle Module involves a 10L scrubbed gas storage tank designed for 7 MPa kept at maximum 4 MPa by a system of spring-loaded pressure regulators. A PPI diaphragm compressor takes suction from this tank and discharges the gas mixture at high-pressure into a 15L buffer tank designed for 35 MPa which serves as a gas feed tank. The recycle gas composition is analysed hourly and calculated ratios of fresh make-up gases are added into the compressor's suction to achieve the desired H_2/CO ratio.

3.3 DATA ACQUISITION

The experimental runs undertaken on the PDU involve continuous operation for periods of 5-7 days during which several sets of parameters are varied according to the experimental program.

Data regarding reaction parameters (pressure, temperature) and product flows corresponding to each set of parameters are monitored continuously. Most stream flows are measured directly and a few are calculated, as shown in Figure 3.2.

Routine periodic analysis of most streams is performed in order to check the correct operation of the system.

Feed/product sampling and weighing procedure allows complete mass balance and product distribution calculations for any time period during a run. Weights and samples are taken throughout the runs on an hourly basis where possible in order to give greater flexibility in the data analysis after the run.

The main streams and sampling points are shown in Figure 3.2 for the general case of gas and solvent recycle. A data acquisition schedule is given in Table 3.1 outlining sample analysis and frequency of analysis as well as the type and frequency of weight or flow measurements.

Feedstock

The coal is sampled from different areas in a 200 kg drum and a composite sample is analysed. A 200 litre drum of starter solvent is heated and mixed well by recirculation of the solvent from the bottom of the drum to the top before a representative sample is taken for analysis. The recycle solvent may be composed of separated liquids and unseparated heavy product. Samples are taken of these as well as a representative sample of the prepared recycle solvent. The feed slurry is usually prepared in 42 kg batches and sampled at least three times from the feed vessel (M2x2) to yield information on water loss from this vessel from evaporation and also to double check that the solids concentration is not too high. The input gas is sampled every two hours and the flow is measured by a D/P cell. When only fresh H_2 is used, the D/P readings are compared to bottle consumption as a double check.

Products

The heavy product is sampled directly from the hot high pressure receiver (M3X1) during a letdown sequence and sent immediately to the lab for solids analysis for a quick indication of the stability of overall reaction. The hot low pressure receiver (M4X5) is emptied every hour and samples taken as required for analysis after the run. The light products receivers (M3X3, M4X6) are emptied every hour and all of these lights are brought to the lab for separation of the water and organic phases. Representative samples of these phases are taken for future analysis.

Five different gaseous product streams are sampled within a two or three hour cycle. The flows are measured on dry gas meters, wet test meters and D/P cells depending on pressures and flow rates. These flow measurement devices are calibrated as required. The least accurate of the flow measurements is the D/P cell where the signal is proportional to pressure and density as well as flow.

A complete set of pressure, temperature and flow readings is taken every hour and a run history of spills, adjustments and equipment behavior is maintained through out the run.

4.0 ANALYTICAL PROCEDURES

4.1 SAMPLING TECHNIQUES

Most materials handled such as feed slurry, heavy product, solvents, eight products and residues are heterogeneous at least at room temperature. Consequently in order to obtain representative samples for analysis these materials must be thoroughly mixed and if required heated above 50°C before a sample is taken.

These samples are either used immediately or they are stored at -17°C until use. In cases when the whole quantity of sample is not used for one analysis the heating and thorough mixing is repeated before aliquots are taken for specific analyses.

The light products which are generally present in two phases are separated into organic and aqueous phases before taking the samples for analysis.

Feed and heavy product samples during the run are obtained directly from process flow lines and considered representative. Samples obtained from storage containers are obtained after heating and sufficient mixing.

Several analyses performed on aliquots of the same sample or from samples taken at close intervals assure consistency in the overall sampling/analysis results.

4.2 METHODS OF ANALYSIS

4.2.1 Determination of Water Content

Determination of water content in the feed slurry and heavy product is done by Xylene azeotropic distillation (ASTM D95-70)

The water in the light product is separated from the organic fraction using a separatory funnel and measured volumetrically with a graduated cylinder.

4.2.2 Determination of Oils, Asphaltenes and Preasphaltenes

Successive soxhlet extractions on the same sample are carried out with three different solvents.

The solubles are defined as follows:

-cyclohexane soluble	
-cyclohexane insoluble/toluene soluble	- oils
-toluene insoluble/tetrahydrofuran soluble	- asphaltenes
	- preasphaltenes

The method allows the following precision:

- cyclohexane soluble determination ± 0.5%
- toluene soluble determination ± 1.0%
- THF extraction ± 0.4%

4.2.3 THF Insolubles by Filtration (for conversion calculations)

THF insoluble content of the heavy product was detemined during the runs by filtration. The method yielded results within 20 minutes of sampling from the continuous unit.

Between 5 and 10 grams of sample were weighed in a beaker and 100 millilitres of THF are added to the beaker. The contents of the beaker are mixed and filtered through two previously weighed glass micropore filters (934-AM) under vacuum on a Buchner funnel. The filters are then dried for 10 minutes at 100°C and weighed. The insoluble content is obtained by difference.

The method yielded precisions of ± 0.6%.

4.2.4 Infrared Spectometry

Infrared spectra were recorded on a Perkin Elmer Infrared Spectrophotometer 700 using a 0.2 mm cell NaCl with methylene chloride as solvent.

The sample (heavy product) was dissolved in methylene chloride 0.30 g in 20 mL solvent and filtered through a syringe.

4.2.5 Vacuum Distillations

Vacuum distillations are conducted using a system described in ASTM D1160-77 with slight modifications. The following cuts are taken:

Fraction I		-	205°C
II	205°	-	275°C
III	275°	-	350°C
IV	350°	-	407°C
V	407°	-	450°C
residue	>450°C		

Reproducibility of the results obtained on anthracene oil are given below:

Fraction	% wt	
I	0.25	± 0.1
II	8.65	± 1.1
III	51.72	± 2.1
IV	29.69	± 0.7
V	5.72	± 0.7
residue	3.82	± 0.6

5.0 OPERATION AND RESULTS

5.1 SUMMARY OF OPERATIONS

5.1.1 Objectives

The objectives of the experiments conducted in this program were the following:

1) Investigate the effect of pressure, temperature, gas liquid flow ratio and time of residence at reaction temperature on the conversion, liquid yield and gas yield obtained from the Estevan lignite and the Roselyne subbituminous coal used.
2) To correlate the results obtained on the continuous unit with results obtained in previous work using a batch autoclave.
3) To verify the versatility of the system, easiness of reaching desired conditions and maintaining stable operation at these conditions.
4) To compare equipment performance at various conditions and assess the mechanical problems connected to the operation of the PDU.
5) To experiment various methods of solids removal for solvent fraction recovery.

5.1.2 Once-Through Experiments

During the 12 months covered by this report, 8 experimental runs divided into 17 experiments were conducted using the continuous system. Over 500 hours of operation were achieved. The operations are summarized in Table 5.1A. Detailed accounts of operations will be presented in the Appendix 1.

The first stage of the experimental program, following the commissioning runs, involved 14 experiments conducted in the once-through mode with raw anthracene oil as solvent (except Exp. No. 6 and 7 when a distillate fraction of heavy product obtained from once-through operation) using Estevan lignite (10) or Roselyne (4) subbituminous coals. The runs lasted 2-4 days during which mass balance and data collection periods of 4-12 hours were conducted.

The gas feed used was hydrogen for all but one experiment which was conducted using a mixture of hydrogen and carbon monoxide.

The first runs (Exp. 3 & 4) were conducted with recirculation of the scrubbed gas. The hydrogen concentration was maintained above 90% volume by addition of fresh hydrogen in the required proportion.

The ranges of operation for the runs conducted in the once through mode are presented in Tables 5.2 and 5.3.

TABLE 5.1A: SUMMARY OF OPERATIONS

Once-Through Experiments

Exp. No.	Date	Type of Coal	Type of Gas	Solvent Used
02	07.04.81	Lignite	H2 recycle	AO[1]
03	08.04.81	Lignite	H2 recycle	AO
04	19.05.81	Lignite	H2 recycle	AO
05	08.07.81	Lignite	H2/CO	AO
06	09.07.81	Lignite	H2	CDl[3]
07	10.07.81	Lignite	H2	CDl
08	18.08.81	Sub-C	H2	AO
09	19.08.81	Sub-C	H2	AO
10	19.08.81	Sub-C	H2	AO
11	20.08.81	Sub-C	H2	AO
15	11.81	Lignite	H2	W[2]
16	11.81	Lignite	H2	W
17	09.03.82	Lignite	H2 recycle	AO
18	12.04.82	Lignite	H2	AO

Recycle Runs

Run No.	Date	Type of Coal	Type of Gas	Start-Up Solvent	Solid Separation Procedure
08	11.81	Lignite	H2	W	filtration
10	09.03.82	Lignite	H2 recycle	AO	distillation
11	12.04.82	Lignite	H2	AO	centrifugation

Notes: 1) AO = anthracene oil (raw)
2) W = Wilsonville hydrogenated oil
3) CDl = distillate fraction of once-through product

TABLE: 5.1B REACTOR CONDITIONS FOR ONE THROUGH RUNS

Exp. No.	02	03	04	05	06	07	08	09	10	11	15	17	18
Temperature °C	425	→	→	→	→	→	→	→	440	→	460	440	→
Pressure MPa	20.7	24.2	→	→	→	→	→	20.8	→	17.9	24.2	→	→
Gas Rate[1]	918	1053	680	520	940	680	1128	598	623	532	463	941	
Mole % H_2	94	94	95	65	100	→	→	→	→	→	→	97	10
LHSV[2] h^{-1}	0.89	0.84	0.87	0.92	0.95	1.43	0.66	1.63	1.58	1.65	0.94	0.98	
Solvent/coal[3]	2	→	→	→	→	→	→	→	→	→	→	→	→
Gas/Slurry[4]	212	242	157	117	250	158	308	153	159	150	176	219	
Type of coal	Lignite	→	→	→	→	→	→	Subbituminous	→	→	Lignite	→	→

Notes:

1) L/H at 20°C and atmospheric pressure
2) Reactor volume = 6.2L
3) kg solvent/kg coal as received
4) L (at 20°C and atm. pressure)/kg initial slurry

SERG

SBRG

TABLE: 5.2 EXPERIMENTAL CONDITIONS FOR ONCE-THROUGH EXPERIMENTS - LIGNITE

Exp. No.	02	03	04	05	06	07	15	17	18
Solvent:									
type	AO →				CD1	CD1	Wilsonville	AO →	
rate (kg/hr)	3.77	3.58	3.73	3.97	4.08	5.9	4.00	4.02	3.11
Solvent/ maf coal	3.07	3.08	3.07	3.07	3.08	3.07	2.95	2.96	3.11
Space rate (kg/hr maf coal - L reactor)	0.20	0.20	0.20	0.21	0.22	0.32	0.23	0.24	0.16
Feed gas:									
rate (L/kg maf coal)	918	1053	680	520	940	680	763	941	750
hydrogen % mole	94	94	95	65	100 →			97	100
Temperatures: (°C)									
slurry preheater	295	297	295	286	294	280	290	300	300
Reactor	425 →							440 →	
Gas separator		247	250	230	220	190	210	250	250
Pressure (MPa)	20.7	24.2	24.8	24.2 →					
LHSV (hr^{-1})	0.89	0.84	0.87	0.92	0.95	1.43	0.94	0.98	0.96

TABLE: 5.3 EXPERIMENTAL CONDITIONS FOR ONCE-THROUGH EXPERIMENTS - SUBBITUMINOUS COAL

Exp. No.	08	09	10	11
Solvent:				
Type	AO →			
Rate (kg/hr)	2.99	7.03	6.71	7.79
Solvent/maf coal	2.7	2.7	2.7	2.7
Space rate (kg maf coal/hr-L)	0.19	0.42	0.40	4.65
Feed Gas:				
Rate (L/kg coal maf)	1128	598	623	532
Hydrogen % mole	100 →			
Temperatures (°C):				
Slurry preheater	280	268	275	276
Reactor	425	425	435	437
Gas Separator	180	197	183	185
Pressure (MPa):	20.8	20.8	20.8	17.9
LHSV (hr^{-1})	0.66	1.63	1.58	1.65

For each set of operating conditions selected, the system was operated at constant flows, pressure and temperatures, and sampling the gas and liquid streams was done hourly. The data collection periods were commenced only after reaching constant conversion results (determined by THF insoluble content of the heavy product in M4X5) and constant gas composition in the M3X3 effluent.

The operation of the system in the ranges tested did not present any significant problems.

Material Balance Considerations

The material balance calculations will be discussed in more detail further in this report. For the majority of the data collection periods the material balance calculated was within ±5 percent which was considered satisfactory.

A large amount of effort was expended in order to provide the correct data for water content in the feed and streams. The problem of the water distribution was recognized and addressed early in the study.

Since the coals used were not dried prior to use, the moisture in the feed is one of the parameters that could potentially influence the mass balance and yield calculations. The slurry blending is done batch-wise after which the slurry is kept for periods of up to eight hours under continuous agitation at temperatures varying between 50 and 80°C. At these conditions moisture is continuously lost due to evaporation and the slurry compositon changes (see Figure 5.1). In order to use the correct water input data, the water content in the slurry is monitored and plotted for the duration of the data collection periods.

In most experiments conducted, water yields in the range of 10% of the maf coal introduced were obtained, due probably to extensive oxygen removal. This seems to indicate that to a large extent hydrogen is consumed to produce water at the reaction conditions tested.

Due to relatively high water input and yield, considerable amounts of water are then present in the reactor effluent.

In the initial concept of the PDU, the first receiver (M3X1) was designed to operate above the critical parameters for water in which case all water would have been collected in the cold receiver M3X2. This condition was modified though, in order to protect the pressure let-down valves, and in all runs undertaken to date, the hot-high-pressure receiver M3X1 was maintained at a temperature in the range of 200 to 250°C. Consequently the water present in the reactor effluent was partially condensed and was then recovered downstream in both the heavy and the intermediate liquid products. The water content of these streams is determined analytically.

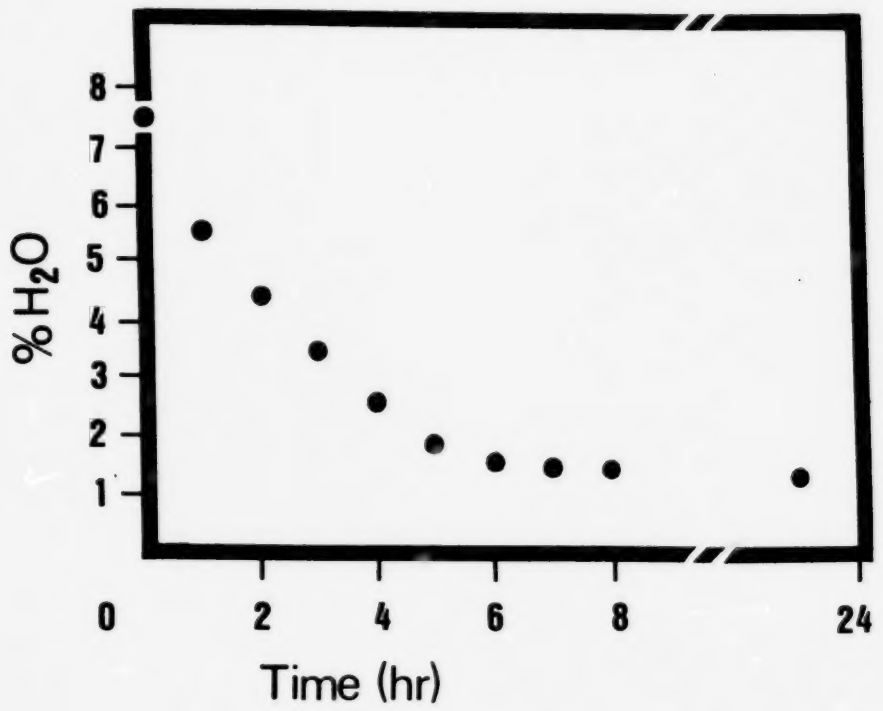


Fig 5.1 Moisture Loss in Slurry with Stirring and Recirculation at 75°C

The results obtained for the once-through experimental program are presented and discussed in Section 5.3.1.

Initial calculations of the space liquid velocities raised concerns related to the probability of solids settling in the reactor.

In practice at the gas/liquid ratios tested there were no indications of solids accumulations in the reactor. This aspect was checked by analysis of the reactor content after blowing down. The explanation may rest with the design of the mixing chamber which provides suitable mixing of the three phases in the reactor, preventing the settling of the solids.

According to calculations using the correlations established by A.M. Shah, B.B. Pruden and J.M. Denis, the voidage in the reactor at our testing conditions is in the 15 to 20% range. This value was confirmed practically by the length of time it takes the liquid to build up at the reactor conditions until it triggers the gamma-ray level indicator in M3X1.

In order to avoid excessive vaporization at the reactor conditions, the expected degree of vaporization was calculated for various gas/liquid ratios and the reactor parameter ranges used (425-440°C and 20-24 MPa), using the data from CANMET Reports 78-4 and 80-23E (D.J. Patmore, B.B. Pruden and A.M. Shah). The gas flow was then selected and maintained accordingly in the range of 10 g mol/kg slurry (7 to 13 gmol/kg) in order to avoid vaporization factors higher than 20% (see Table 5.1B).

5.1.3 Solvent Recovery and Recycle Runs

After completion of six runs conducted in the once-through mode, the data collected was analysed and preliminary results indicated satisfactory levels of conversion of lignite into liquid products. The program then proceeded to the next step; extended runs using a fraction of the liquid product as solvent for the coal slurry.

Preliminary laboratory testing results as well as data provided by the two once through experiments using a distillate fraction as solvent (Exp. No. 6 and 7) were used in establishing a program for the study of solvent recovery.

The initial design of the PDU provided for vacuum distillation of the heavy product (M4X5) in order to produce a solids free coal derived fraction to be used as solvent.

Early in the study it was recognized that this concept was by far too rigid to allow the degree of versatility required for optimization of the solvent recovery step. Also, the lack of back up in case of failure of the existing distillation unit was a cause of concern.

Other methods for solids removal were tested first in the laboratory, then in the continuous system. These methods were: filtration, distillation, and centrifugation (hydroclones and centrifuges). None of the above used alone gave full satisfaction and the conclusion drawn was that optimum solvent quality as well as a positive balance in solvent production will be obtained by the combination of streams obtained by using these or other methods in suitable sequence.

The approach used in selecting the methods for solvent recovery was to obtain, for recycle, a liquid fraction containing less than 8% of THF insolubles and which was heavy enough to avoid excessive vaporization at reactor conditions.

In order to establish base cases for further comparison, three runs were conducted with Estevan Lignite, hydrogen gas and using as recycle solvent a fraction of the product separated by one of the following methods:

Run No. 8 - Filtration
Run No. 10 - Vacuum distillation
Run No. 11 - Centrifugation.

In order to ensure solvent balance, the recycle solvent in all three runs was a combination of solids-free liquid and unmodified product from M4X5.

The objectives of the extended recycle runs were:

- to achieve ten passes through the system, maintaining solvent balance and stable operation of the unit,
- to produce sizeable amounts of true coal-derived products to be analysed and used at a later date,

- to observe the equipment performance at the conditions of extended operation,
- to assess the evolution of feed and product qualities when coal-derived product was recycled,
- to check for ash or solids accumulation in the reactor,
- to monitor trends in conversion, liquid, gas distillable yields and accumulation of asphaltene and preashphaltene component in the heavy product.

Not all of these objectives were successfully realized.

The first of the recycle runs was Run No. 8 (experiemtns 16-01 - 16-10). The goal was to recycle a mixture of approximately 1/1 solids free filtrate and M4X5 product non filtered, aiming to maintain the solids content in the solvent between 5 and 8%.

Ten passes were completed in spite of some technical and equipment problems encountered. The filtration of M4X5 product was increasingly difficult with the number of passes reaching the point after six passes when the filtration rate was too low to allow the completion of filtration in the time available. The unfiltered portion of the solvent recirculated increased after the second pass until the solvent used in the seventh pass and from there on, was unfiltered M4X5 with solids contents (THF insoluble) increasing gradually.

The run was considered a limited success and allowed for some conclusion to be drawn, such as:

- Recirculation of some solids back into the system is beneficial for the conversion.
- The viscosity and stickiness of the product increases with the number of passes making the straight vacuum filtration an unlikely route to solids removal.
- The fact that the amount of solids in the solvent had to be allowed to exceed the proposed 8% introduced an additional variable in the test which interfered with the reaching of a steady state. Nevertheless definite trends in conversion and asphaltene production were observed.

Ten passes were completed in the second run with recirculation (Run No. 10) using vacuum distillation for solids removal, recycling as solvent a combination of 250°C - 420°C range distillate and unmodified M4X5 product. The THF insoluble content in the solvent was maintained below 8%, the solvent balance was good and there were no operational problems during the 72 hour run.

The conversions calculated over each pass were generally higher than in once through experiments, with peaks above 90% (95% average pass 5-9) maf organic (including fresh coal and recycled solids), good total liquid yields were obtained (55.5% to 70.8% with an average 68.4%) over the 5-9 passes.

Determinations of cyclohexane soluble material in the heavy oil (M4X5 product) gave results above 75% peaking at 81.0%. A detailed discussion of the results is presented further in this chapter. The results obtained in this run will constitute a good base-case for comparisons of results where other solids separation methods will be used.

A third run with recirculation of solvent was undertaken in order to test the product quality and yields when the liquid recycled as solvent was a combination of centrifuge overflow and unmodified M4X5 product.

The centrifugation was conducted at temperatures above 90°C, under nitrogen atmosphere, using a semi-continuous centrifuge at 2500 r.p.m. Details of the operation will be given later.

About 75% of the centrifuge feed was collected in the overflow. The solids (THF insoluble) content in this stream increased gradually from 0.22% to 15.12% over seven passes through the system which is one of the factors accounting for the deterioration of the separation efficiency in the centrifuge.

The viscosity of the product increased gradually with the number of passs through the system. With the viscosity increase the separation efficiency decreased in the centrifuge. A second factor accounting for the deterioration of the efficiency was probably the reduction in the size of the solids particle after multiple passes through the system.

The centrifuge cake contained about 50-58% solids and it was "drier" towards the bottom and "wetter" towards the top of the bowl.

The heavy product obtained in the pass No. 7 was very viscous and "sticky" and contained 20% solids. In view of the poor separation obtained at the prior centrifugation (after the pass 6) this product was not centrifugated any more. At this point in the experiment it was decided to test the further conversion of this material when reintroduced in the reactor, without addition of fresh coal, maintaining the reactor parameters constant. The results will be discussed in detail in the section 5.7 of this report.

The heavy fraction of the product obtained in this way appeared somewhat more fluid, the solids content decreased to 17% THF insoluble. One additional pass through the system was achieved using this material mixed with a small amount of red mud (basis of calculation addition of Fe_2O_3 in proportion of 10% maf). Detailed results of these tests are presented in section 5.7. Further conversion of the remaining organic material into liquid was obtained in each of the final passes.

5.2 DEFINITIONS AND DATA HANDLING

As described in Section 3.3 on data acquisition, feed/product samples and weights as well as operating conditions are taken throughout a run. The first step in data handling involves plotting all of the relevent readings

and lab results for the total run. Steady conditions are then chosen to define the start and end times of the individual experiments. An amount of slurry equivalent to about three reactor volumes is required before steady conditions are attained after a parameter has been changed. This data collecting period usually lasts three to five hours.

5.2.1 Data Requirements

The following data was used for mass balance and yield calculations:

Feedstock

batch preparation
- coal - weight, % H_2O Content, ash content
- solvent - weight, % H_2O, % THF insolubles

feed vessel
- load cell readings versus time
- % H_2O determined at least three times per batch

gas
- D/P flow counter reading versus time
- gas chromatography analysis if recycle gas is used

Product

heavy product
- mass flow (every hour)
- % THF insolubles determined on sample from hot high pressure receiver (M3X1) every hour
- % H_2O on composite samples

light products
- mass flow (every hour)
- (the product collected is physically separated into water and organic fractions and weighed).
- % THF insolubles if necessary.

gases
- flow readings taken every hour or less and gas analysis done on two hour cycle on the following streams:
  - M4X5 off gas
  - M3X3, M4X6 off gases
  - unscrubbed gas
  - scrubbed gas
  - M5X1 off gas
  - M6X1 vent gas

5.2.2 Material Balance Calculations

Gas Stream Calculations

All streams are analysed for the following:

H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, H_2S

NH_3, and C_4+ components are considered. The chromatograph data is calculated using external and internal normalization methods and results are checked for consistency. Molecular weight of the gases and percent weight of each component are calculated from the G.C. analysis.

Each stream is regularly monintored for flow and volumes are plotted against time. A least squares fit of volume vs time is done and total volume per experiment for each stream is calculated. Mass flow rates and total component weight for each stream is calculated from the G.C. and flow data.

Non-gaseous Streams Calculation

The following calculations are made using the load cell readings versus time and % H_2O analysis for the feed vessel (M2X2):

1) The batch preparation weights and the coal solvents analysis are used to calculate the feed composition on a moisture free basis as follows:
   - % ash
   - % m.a.f. coal
   - % THF soluble solvent
   - % recycle insoluble organics (for recycle mode only)
2) The % H_2O analysis vs batch time is used to determine the average % H_2O in the feed vessel
3) The feed composition is then recalculated on a wet basis using this average water content
4) The load cell readings (corrected for sampling and eventual spills) and water analyses are then used to calculate the amount of water lost from the vessel by evaporation. Ths is subtracted from total weight loss as determined from the load cell readings to obtain a net weight fed to the reactor
5) Net component weights and flow rates are then calculated.

The heavy product collection weight and time data was corrected for sampling and spills and a least squared fit was done. The experiment start and end times were then used to calculate total heavy product weight and flow rate. An average % THF insoluble content and a % H_2O analysis of a composite sample were used to calculate the heavy product composition and net weights. Apriori was adopted the assumption that ash IN equals ash OUT. This is based on the fact that no solids accumulation in the system was observed during any of the tests. Ash analysis was conducted mostly for the solids separation evaluation, not for the material balance purposes.

The light product from M4X6 and M3X3 are separated into water and organic fractions and the weights were plotted versus time to obtain the compositions and weights.

The mass balance was forced to 100% on total input including gases vs total output, and unless there was reason to believe that a certain output weight was in error, prorating was done proportionally on all product streams.

5.2.3 Definitions of Conversions and Yields

Conversions and yields are calculated on both a moisture free (m.f. coal) and a moisture and ash free (m.a.f. coal) basis.

Conversion

$$\text{coal conversion} = \frac{\text{kg m.a.f. coal} - \text{kg (THF insolubles} - \text{ash out)}}{\text{kg coal input*}}$$

Yields

$$\text{liquid yield} = \frac{\text{kg organic liquid out} - \text{kg solvent IN}}{\text{kg coal input*}}$$

water=(water out - water in)/ kg coal input

gas yields

H_2 = (kg H_2 out - kg H_2 in)/kg coal input*

CO_2 = (kg CO_2 out - kg CO_2 in)/kg coal input*

etc.....

distillate yeilds

(kg product cut - kg solvent cut)/kg coal input*

* coal m.f. or m.a.f.

The water and liquid yields are very sensitive to water content in the feed and in the products. As mentioned above, the water evaporated from the feed vessel and hence not fed to the reactor was accounted for by sampling the feed at least three times during a batch and analyzing for water. The water in the products was determined for several samples and an average value was used in calculation.

As an indication of the sensitivity of liquid yield calculations to water determination it is noted that a 1% error in water content in the feed or product results in a 4% error in conversion or liquid yield values.

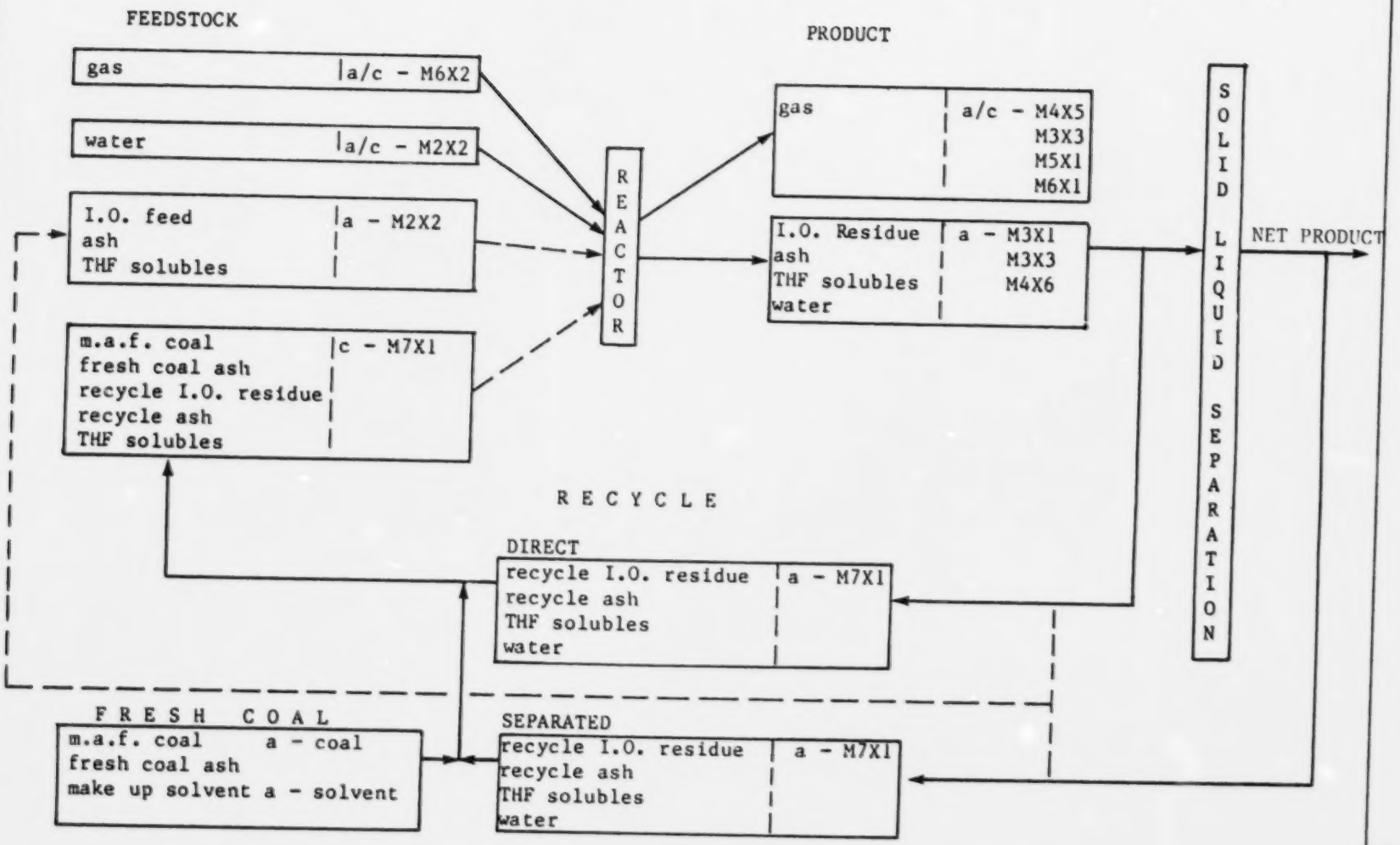
For these reasons, several feed and product samples were taken during an experiment in order to minimize errors. An average value is taken for the individual experiments.

For the recycle experiments, a breakdown of the feed and products is given in Figure 5.2 which should be studied in conjunction with Figure 3.2 where data acquisition points are given.

The water in the feed slurry is determined in the same manner as described above for the once-through experiments. The "dry" feed slurry can be analysed for THF insolubles and ash content in the feed vessel or broken down into fresh coal and ash, recycle insoluble organic residue and ash and THF solubles by analyzing each component making up a batch.

Data collection period for a recycle "pass" is usually commenced at least 4 hours after the start of a batch when operations conditions and THF insolubles contents in the product are considered stable.

Figure: 5.2 SBRG Continuous Unit
Recycle Mode Data Analysis



I.O. - insoluble organic
a - analysis
c - calculation

Conversion and yields are calculated relative to insoluble organic feed or relative to fresh coal, depending on the extent of analyses carried out for the individual batches.

In these preliminary recycle runs, a steady state operation generating a recycle solvent of constant composition was not attained. In order to appreciate the behaviour in the process of the fresh coal only, (as opposed to total THF insoluble organic matter), certain assumptions were required.

At steady state operation, where the solvent composition is constant both in terms of chemical structure and in content of recycled solids, it can be correctly assumed that the net product of the plant is generated only from the fresh feed and yield calculations can be based on the amount of coal fed per unit of time. In the recycle runs where the concentration and composition of the recycled solids varied from one pass to the next and at the same time the amount of fresh coal fed per unit of time varied from one pass to the next, it is not possible to differentiate the net product generated from fresh coal from the net product generated by further conversion of the recycled solids. In order to overcome this difficulty, two independent assumptions are possible:

a) that the fresh coal will convert to the same extent in the recycle passes as it did in the first pass with the starter solvent;
b) that the recycled THF insoluble organic fraction will convert to the same extent in all pases. It is possible to qualify this conversion by passing a recycle solvent containing a determined amount of organic solids through the reactor without any fresh coal and analyse the product.

Obviously each one of these assumptions has its' drawbacks.

For the calculations presented in this report, the second assumption was adopted. The rate of conversion for the recycled THF insoluble organic matter was determined in one of the subsequent runs (Run No. 11) by recycling the heavy product obtained in pass 7 (without removing any solids and without adding any fresh coal). The conversion and liquid yield calculated in this test were 37.5% wt. maf recycle IOR (THF insoluble organic residue) and 12.1% wt. maf recycle IOR, respectively. If it is assumed that recycled organic insolubles will behave similarly in all passes through the system, it is possible to calculate the conversion and liquid yield for fresh coal only by subtracting from the gross yield the prorated value corresponding to the amount of recycled IOR in each pass.

5.3 FEEDSTOCK CHARACTERIZATION

The two coals used in the program were part of the same shipments used in the first phase of the project. The coals had been ground in 1980 (to 100% passing through -200 mesh) and were stored until use in plastic lined 55 gal. drums under inert (CO_2) atmosphere. The possibility of aging and/or some oxidation of the two coal samples is not discarded.

The coals have been analysed for moisture and ash content, elemental composition and volatile matter in the SBRG laboratory and petrographic analysis was conducted by Dr. Judith Potter of the Department of Geology, University of Regina. Tables 5.4 and 5.5 present the coals analyses.

Table 5.6 presents the analyses of the materials used as solvents in the once-through runs and as start-up solvents in the recycle runs.

Three 1000 litre lots of anthracene oil lots were purchased from Crowley Tar Products Co., Inc. The oil was transported and stored in 55 Gallon drums and it was a nonhomogeneous dark material at room temperature settling a semi-solid layer on the bottom. When heated above 50°C and mixed, the material became a nonviscous homogeneous liquid. The fractionate distillation of samples from the three lots gave slightly different results but the elemental composition was very close.

The coal derived fraction (CDI) used for experiments No. 6 and 7 in the once-through Run No. 5 was a lighter material than the initial anthracene oil as indicated by the fractionated distillation, but having an elemental composition very similar to that of the anthracene oil.

Two 55 gallon drums of hydrogenated oil were obtained from the Wilsonville SRCI pilot to be tentatively used as start-up oil in Run 8 and 9. This solvent is very much different both in distillation curve (20% distills below 270°C) and elemental composition (9.5/9.8% hydrogen content). It was a nonviscous homogeneous liquid at room temperature.

5.4 DISCUSSION OF ONCE-THROUGH LIQUEFACTION RESULTS

The tests conducted during this contract, fourteen in the once-through mode and three in the solvent recycle mode, provided the first systematic information on the operation of the PDU and also the first extensive data regarding liquefaction of the Estevan lignite in a continuous system.

The data accumulated over the 500 hours of operation of the PDU regarding the performance of the system itself, the trends in yields and quality of products, correlation of reaction parameters and coal conversion are considered the main results of the work undertaken.

The equipment performance will be presented in Section 6 and considerations related to the liquefaction results will be presented in the data analysis which follows.

The total conversion, hydrogen consumption, organic liquid, water, and gas yields are considered in relation to operating parameters such as:

- CSV coal space velocity (kg/h x liter of reactor volume)
- LHSV liquid hourly space velocity (h^{-1})
- S/C solvent to coal ratio (kg/kg maf coal)

TABLE 5.4: ULTIMATE & PROXIMATE ANALYSIS OF COALS

	ESTEVAN LIGNITE	ROSELYNE SUB-BITUMINOUS - C
PROMIMATE ANALYSIS (%)		
MOISTURE (OVEN)	21.8	11.4
MOISTURE (XYLENE)	22.98	13.7
VOLATILE MATTER	39.9	47.8
FIXED CARBON	21.3	27.2
ASH (MF BASIS)	17.0	13.6
ULTIMATE ANALYSIS (%)		
CARBON	59.3	60.1
HYDROGEN	4.1	5.01
NITROGEN	1.8	3.65
SULFUR	1.1	0.54
OXYGEN (BY N-ACTIVATION)	16.7	17.1
ASH	17.0	13.6
H/C	0.83	1.00
ASH ANALYSIS (ppm)		
Al	94000	88000
Co	25	22
Cu	60	212
Fe	48000	91000
Li	-	-
Mg	16300	11300
Ni	38	114
K	1460	2980
Na	19500	6900
Sn	80	80
Va	30	28
Mo	10	15

TABLE 5.5 PETROGRAPHIC ANALYSIS OF COALS

	ESTEVAN LIGNITE		ROSELYNE SUB-C	
Vitrinite/Huminite	77.3	75.0	94.0	92.2
Sporinite		2.0	0.75	1.0
Resinite		2.0	0.25	0.8
Cutinite	3.8	-	-	0.2
Liptodetrinite		1.0	0.25	0.2
Fusinite		0.2	1.0	0.4
Semifusinite	17.5	11.0	1.0	0.4
Semimacrinite		0.8	-	-
Inertodetrinite		6.0	1.0	1.6
Mineral Matter	1.4	2.0	1.75	3.2
	100 %	100 %	100 %	100 %
Summary				
Vitrinite/Huminite	77.3	75.0	94.0	92.2
Liptinite	3.8	5.0	1.25	2.2
Inertinite	17.5	18.0	3.0	2.4
Mineral Matter	1.4	2.0	1.75	3.2
	100 %	100 %	100 %	100 %
Reflectance				
Average % R_o random	0.37	0.37	0.39	0.39
Std. Dev.	0.05	0.05	0.06	0.06
Reactives:Inerts Ratio		5.12		
Vitrinoid type		3.0		

TABLE 5.6: SBRG ANALYSIS OF SOLVENTS

ANALYSIS	ANTHRACENE OIL LOT #1	ANTHRACENE OIL LOT #2	ANTHRACENE OIL LOT #3	WILSONVILLE SOLVENT BARREL #1	WILSONVILLE SOLVENT BARREL #2	COAL DERIVED SOLVENT #1
% H2O (XYLENE)	-	0.12/0.12	0.2/0.20	0.40	0.29	-
% THF INSOLUBLE	-	0.01/0.11	0.01	-	-	-
% BENZENE INSOLUBLE	-	0.247/0.360	-	-	-	-
% HEXANE INSOLUBLE	-	-	-	-	0.14	-
DENSITY	1.109 at 20°C (pichnometer)	-	-	0.9120 at 21°C 3) (API)	0.9813 at 21.75°C 4) (API)	-
VISCOSITY	5.869cst at 1) 54.5°C 2.16cst at 98.9°C	-	-	-	23.5cps at 20°C 10cps at 45°C 2)6.7cps at 59.5°C	-
ELEMENTAL ANALYSIS						
% C	90.8	91.1	91.4	89.4	89.0	91.1
% H	5.8	5.7	6.0	9.8	9.5	6.3
% N	0.9	1.00	1.0	0.8	1.00	0.90
% S	-	0.6	0.7	0.0	0.0	0.5
% O (by Difference)	2.5	1.6	0.9	nil	0.5	1.2
% O (Neutron Activation)	-	2.0	-	-	-	1.68
H/C	0.77	0.77	0.79	1.28	1.28	0.82
Distillation (% by wt.)						
200°C		I.B.P 135°C 3.5	0.2	I.B.P. 195°C 1.7	I.B.P. 195°C 1.7	I.B.P. 230°
200 - 270°C		12.0	8.6	17.9	18.7	16.2
270 - 300°C		7.0				
300 - 350°C	66.1	40.9	51.4	36.7	36.1	61.6
350 - 400°C		26.6	29.9	23.7	23.7	16.4
400°C +	to 409°C 27.1	to 412°C 4.5	to 450°C 6.6	to 493°C 18.9	to 498°C 19.1	to 420°C 3.5
RESIDUE	6.8	5.5	3.3	1.1	0.7	0.3

1) Kinematic viscosity
2) Apparent Viscosity
3) 12.6 at 21°C
4) 12.7 at 21.75°C

note: the dash signifies "not analysed"

- T average reactor temperature (°C)
- P operating pressure (MPa)
- G/L gas to slurry ration (LSTP/kg)

A summary of results obtained in the tests conducted in once-through mode is presented in Table 5.7.

Reproducibility of Results

During the program a total of 10 tests were conducted on lignite, three sets of two tests were under conditions which were sufficiently similar to examine the test results for reproducibility. The conditions of the six tests compared are as follows:

	Experiment					
Conditions	03	04	15	16	17	18
Solvent	Anthracene Oil		Wilsonville		Anthracene Oil	
Temperature°C	425		425		440	
Pressure MPa	24.2		24.2		24.2	
LHSV (hr^{-1})	0.85	0.88	0.99	0.99	0.98	0.72
Results(% maf)						
Conversion	84.5	84.3	85.7	83.5	84.9	82.8
Liquid yield	64.2	58.8	50.1	49.1	63.5	59.0
C_1-C_3 yield	4.6	4.6	7.5	5.7	3.7	4.4
H_2O, CO/CO_2 yield	16.4	22.1	28.9	28.6	22.4	21.2

Duplicate tests conducted with two solvents and at 2 temperature levels showed excellent repeatability.

Effect of Reaction Time

In terms of conversions obtained when lignite was used, two effects appear significant, the hourly liquid space velocity and the hydrogen partial pressure.

Lower space velocities favour higher conversions probably due to the kinetic effect of increased residence times as shown in Figure 5.3. When only H_2 was used conversions above 80% were calculated for all tests conducted at LHSV below 1.0 h^{-1} and reactor pressure of 24.2 MPa.

A similar effect of the liquid space velocity was found in the subbituminous coal testing. Conversion of 87.4% corresponded to the lower LHSV (0.7 h^{-1}) and 65.5% to the higher (1.66 hr^{-1}) LHSV at the same pressure and temperature. This effect is somewhat attenuated at higher temperature when conversions of 77 and 81.4% were obtained.

The liquid yield (THF solubles) data is presented in Figure 5.4.

TABLE 5.7 ONCE-THROUGH EXPERIMENTS - SUMMARY OF RESULTS

Exp No.	Type of Coal	Type of Solvent	LHSV h-1	C/L kg maf coal x100 / kg slurry	G/L LSTP/kg slurry	P MPa	T °C	Conversion to THF solubles % maf coal	H2 Consumption % maf coal	Organic Liquid yield % maf coal	H_2O yield % maf coal	($CO+CO_2$) Yield % maf coal	C1-C3 yield % maf coal
02	Lignite	AO	1) .88	23.1	212	20.7	425	77.3	n.a.	61.2	n.a.	6.4	2.1
03	Lignite	AO	1) .85	23.0	243	24.2	425	84.5	1.3	64.2	10.7	5.7	4.6
04	Lignite	AO	1) .88	23.1	157	24.8	425	84.3	1.2	58.8	12.2	9.9	4.6
05	Lignite	AO	1) .93	22.7	117	24.2 H2/CO=2/1	425	76.5	1.3 (H2) 13.6 (CO)	67.3	(16.7)	20.4	6.5
06	Lignite	CDI	4) .96	23.1	217	24.2	425	82.9	1.2	70.1	0.2	8.9	4.6
07	Lignite	CDI	4)1.41	23.4	159	24.2	425	78.3	1.0	60.6	3.4	10.1	4.2
15	Lignite	W	5) .99	23.1	176	24.2	425	85.7	2.3	50.1	20.9	8.0	7.5
16	Lignite	W	5) .99	22.5	172	24.2	425	83.5	1.9	49.1	22.8	5.8	5.7
17	Lignite	AO	3) .98	23.3	219	24.2	440	84.9	5.1	63.5	11.0	11.4	3.7
18	Lignite	AO	3) .72	22.1	166	24.2	440	82.8	2.8	59.0	15.2	5.9	4.4
08	Sub-C	AO	2) .70	27.3	308	20.8	425	87.4	3.8	60.3	17.2	8.0	5.7
09	Sub-C	AO	2)1.66	25.7	154	20.8	425	65.5	3.2	43.5	13.5	8.4	3.2
10	Sub-C	AO	2)1.59	25.5	148	20.8	435	77.0	2.9	44.4	19.6	9.8	6.1
11	Sub-C	AO	2)1.68	28.2	150	17.9	437	81.4	2.4	55.7	12.7	10.3	5.4

Notes: 1, 2, 3 Anthracene oil lot N = 1, 2 and 3
4 CDI - Distilled fraction of once through lignite derived product
5 W = Wilsonville hydrogenated solvent

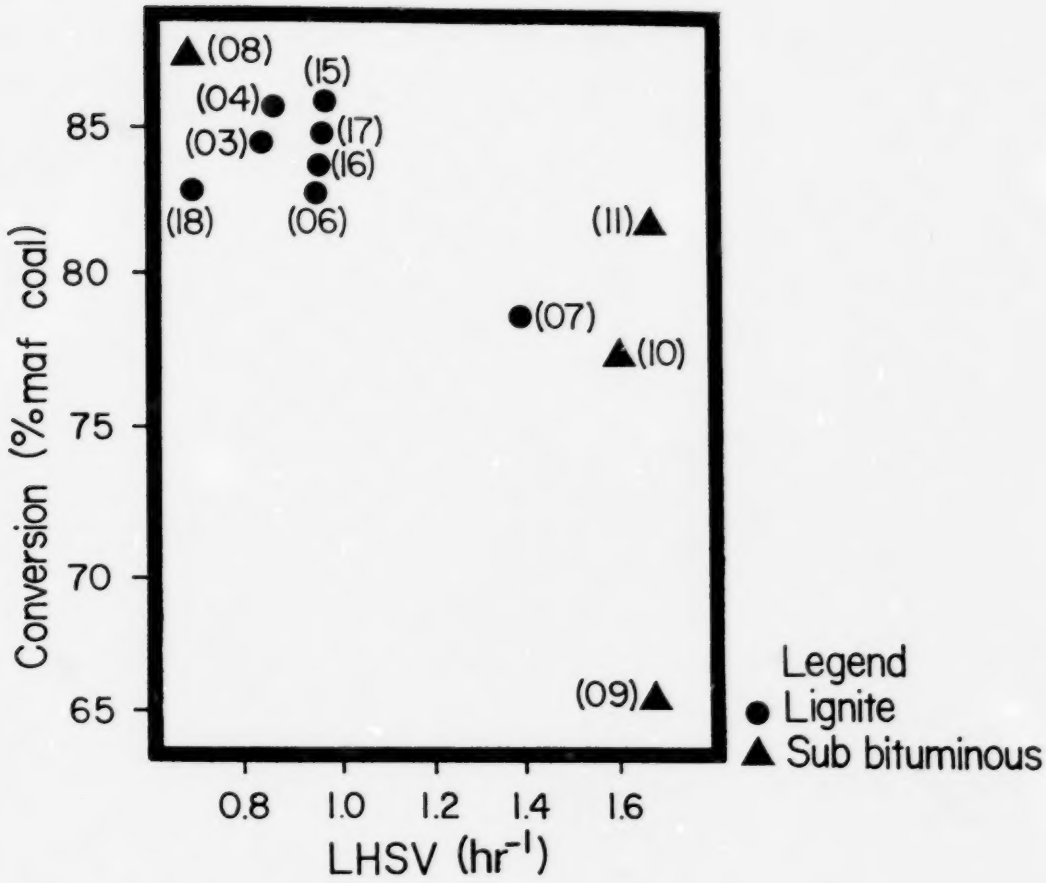


Fig 5.3 Conversion
Once-Through Tests

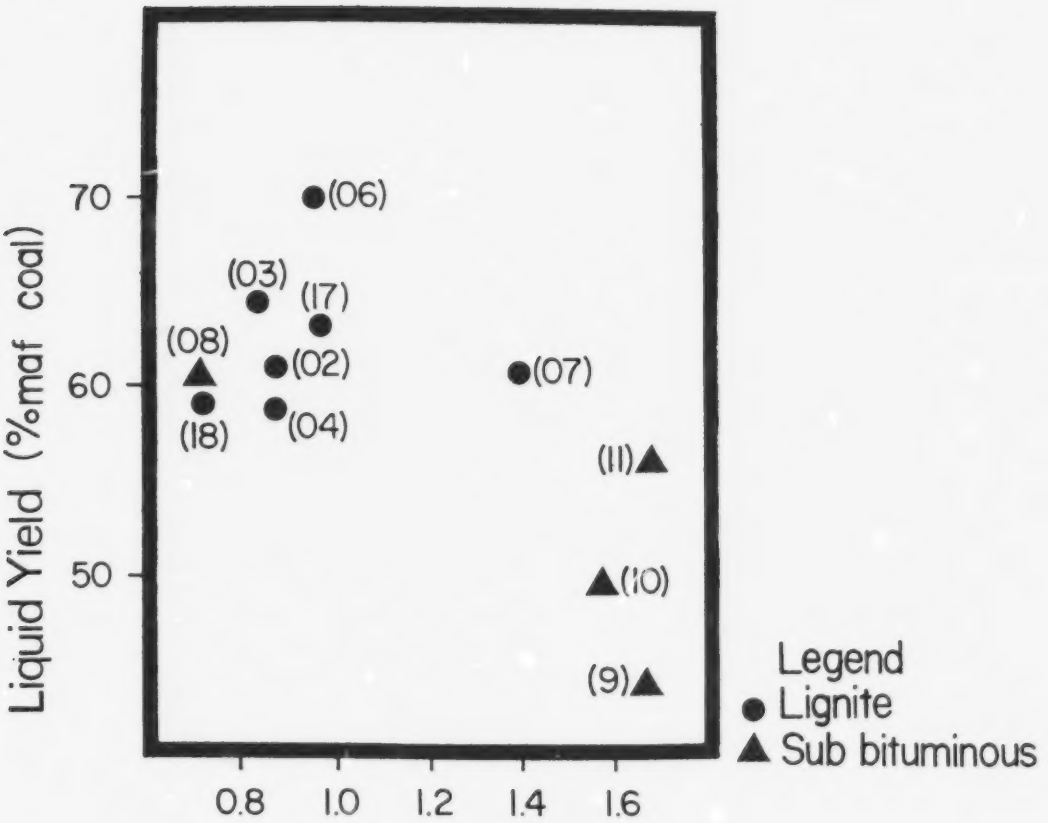


Fig 5.4 Liquid Yields

Once-Through Tests

Sub-bituminous Coal Results

The conversions obtained with subbituminous coals are low compared to literature data (9), (10), but probably this may be explained by the unusual structure of this particular subbituminous coal sample, as presented in the petrographic analysis (Table 5.5).

Syngas Results

The results obtained where a mixture of carbon monoxide/hydrogen (30/70 V/V) was used as reducing agent (Exp. 05) were surprisingly low as shown in Table 5.7. Previous work by SBRG (1, 2,) and other research groups on lignite using CO/H_2 mixtures indicated higher conversions. The high liquid yield and CO/CO_2 yield obtained in this test indicate a high degree of deoxygenation which concurs with the assumption that carbon monoxide has a scavenging effect on the oxygen present in the lignite. This test should be repeated as the effect of CO/H_2 mixtures warrants further investigation.

Effect of Solvent

A strong effect of the solvent used is evident not so much in the conversion results but in the organic liquid yields and deoxygenation through production of water and carbon oxides. The two tests conducted with the Wilsonville hydrogenated solvent resulted in high conversions (83.5 and 85.7% maf coal) but relatively low liquid yields (50.1 and 49.1% maf coal) the water make was unusually high (20.9 and 22.8% maf coal) and the total gas yields were in the order of 15%.

The presence of some coal derived material in the solvent was found to improve the liquid yield by about 5%. This observation was confirmed in the early passes of the recycle runs.

No other clear trends are discernible and the interplay between the physical parameters (LHSV and G/L) and kinetic variables (P and T) is inconclusive. A general observation is that with the exception of the two tests conducted with Wilsonville solvent, the lignite yielded 60 to 70% maf coal in liquid product and in addition to that 5-10% gaseous hydrocarbons.

In the tests with lignite it was apparent that the type of the solvent used had a considerable effect on the hydrogen consumption. The three solvents used show a different behaviour in so far as anthracene oil seems rather refractory to hydrogenation and subsequent hydrogen transfer as compared to the Wilsonville solvent or the coal derived distillate CD1. Higher space velocities resulted in lower H_2 consumption while the higher gas/liquid ratio resulted in an increase in the H_2 consumption.

Hydrogen Consumption

The hydrogen consumption was determined on the basis of gas measurements, thus the accuracy of values calculated increased with the improved gas flow measurements.

Product Characterization

Elemental analyses of the feed and various product fractions are presented in Table 5.8. The data contained here should be used in establishing trends only since the solvent interference makes it difficult to discuss the composition of the coal-derived products.

From the H/C atomic ratio it would appear that little hydrogenation of the coal takes place in addition to the initial, relatively easy and fast depolymerization step leading to significant conversions to THF solubles.

It would suggest that H_2 is taken up to induce hydrocracking reactions and extensive deoxygenation. Both actions are consistent with the observed data for C_1-C_3 formation.

Qualifications of the extent of the deoxygenation of the organic liquid product was not possible due to the errors in determining oxygen content by difference.

The production of 15-20% of H_2O and CO/CO_2 indicate that deoxygenation of the coal does take place in the range of reaction parameters tested. The oxygen content determinations done by neutron activation on some of the product fractions resulted in values of 2-3% oxygen for distillate fractions compared to 5-6% in the slurry feed.

On the basis of the elemental analysis of the products it appears that sulphur is removed mostly as H_2S, without a clear trend being evidenced in the liquid products.

A more indepth analysis of the results obtained in the once-through mode does not seem warranted due to the presence of large proportions of the solvent used and the unknown extent of the solvent reactions at the reaction conditions in the presence of the coal.

5.5 DISCUSSION OF RECYCLE RUNS

The three recycle runs conducted in this program were started with extraneous solvents (anthracene oil for Runs Nos. 10 and 11 and Wilsonville hydrogenated solvents for Run 8). The first feed batch for each run was prepared using the start-up solvent and coal. The liquid product obtained during the first 7 hours was used for preparation of the feed for the next pass.

The solvent recycle procedure adopted was to collect the heavy oil produced over a period of usually 4-5 hours and subject the composite to the solids separation method selected. The solids free liquid obtained was then mixed with heavy oil produced in the next 3-4 hours and the mixture was returned as solvent to the slurry preparation module. This procedure allowed for recycle of a part of the ash and unconverted coal as well as partial recirculation of the condensed polycyclic aromatics contained in the heavy product. The

TABLE 5.8 ONCE-THROUGH EXPERIMENTS - ELEMENTAL ANALYSIS RESULTS

Exp No.	Sample Analysed	% weight of Total Liquid Feed	% wt C	H	N	S	O by diff	O N. Act.	Ash	H/C
2.	Feed	100	82.5	5.57	0.75	0.79	5.99	n.d.	4.4	0.81
	M3X3(organic phase)	0.4	87.28	9.48	0.79	0.62	1.83	2.47	-	1.30
	M4X6	14.6	77.2	5.99	0.87	0.76	11.49*	n.d.	3.69	0.93
	M4X5 total	80.73	83.5	5.70	0.90	0.68	4.92	n.d.	4.0	0.82
	Dist.fr. < 275°C	10.82	90.5	7.22	0.86	0.49	0.93	2.44	-	0.96
	275 - 350°C	28.82	90.1	6.26	0.62	0.70	2.32	2.47	-	0.83
	350 - 405°C	17.03	91.8	5.73	1.30	0.53	0.64	1.39	-	0.75
	405 - 450°C	6.62	89.5	5.79	1.48	0.63	2.60	n.d.	-	0.78
	Residue 450+	17.44	69.3	3.95	1.92	0.66	5.64	n.d.	18.53	0.68
3.	Feed		79.6	5.56	0.79	1.12	8.58	n.d.	4.35	0.83
	M3X3(organic phase)	.4	87.33	9.31	0.50	0.53	2.33	n.d.	-	1.28
	M4X6	16.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	0.93
	M4X5 total	76.4	83.7	5.70	0.92	0.71	5.97	n.d.	3.0	0.81
	Dist.fr. < 205°C	2.02	85.0	9.1	0.56	0.80	4.54	n.d.	-	1.28
	205 - 275°C	9.54	87.2	6.98	0.66	0.47	4.69	n.d.	-	0.96
	275 - 345°C	28.88	90.5	6.36	0.52	0.74	1.88	n.d.	-	0.84
	345 - 407°C	15.13	92.1	5.61	1.03	0.45	0.81	n.d.	-	0.73
	407 - 475°C	4.90	88.0	6.26	2.02	0.71	3.01	n.d.	-	0.85
	Residue 475+	15.93	67.9	4.13	2.04	0.85	10.69	n.d.	14.39	0.73
4.	Feed		83.85	5.99	0.83	0.61	4.23	n.d.	4.49	0.86
	M3X3(organic phase)	0.7	82.03	9.35	0.61	0.51	7.5	2.64	-	1.37
	M4X6	26.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.93
	M4X5 total	66.45	82.2	6.0	1.11	0.60	6.2	n.d.	3.89	0.73
	Dist.fr. < 205°C	6.90	78.2	7.52	0.35	0.48	13.45*	8.53	-	1.15
	205 - 275°C	5.88	90.2	7.41	0.27	0.44	1.68	2.63	-	0.99
	275 - 350°C	39.82	89.9	6.22	0.55	0.62	2.71	2.21	-	0.83
	350 - 405°C	16.32	89.6	5.65	0.93	0.56	3.26	1.93	-	0.76
	405 - 450°C	6.11	88.8	5.59	1.28	0.59	3.74	5.08	-	0.76
	Residue 450+	18.23	67.1	4.24	1.31	0.91	2.64	n.d.	23.8	0.76

TABLE 5.8: (continued)

Exp No.	Sample Analysed	% weight of Total Liquid Feed	% wt C	H	N	S	O by diff	O N. Act.	Ash	H/C
5.	Feed		81.4	5.49	1.30	0.78	6.53	n.d.	4.5	0.81
	M3X3(not analysed)	0.4								1.3
	M4X6 " "	9.6								
	M4X5 total	83.54	86.0	5.78	1.28	0.62	1.62	n.d.	4.7	0.93
	Dist.fr. < 205°C	1.6	82.7	9.07	0.79	0.55	6.89	n.d.	-	0.81
	205 - 275°C	12.9	85.1	6.66	0.78	0.41	7.05	2.85	-	1.31
	275 - 350°C	19.8	90.5	6.73	0.44	0.71	1.62	2.86	-	0.94
	350 - 452°C	25.7	91.6	5.66	0.96	0.65	1.13	1.75	-	0.89
	Residue 452+	20.0	65.9	4.12	1.16	0.67	9.14	n.d.	19.05	0.74
6.	Feed	100	82.5	5.86	1.06	0.62	4.86	n.d.	5.1	0.75
	M3X3(organic phase)	.5	80.9	8.61	0.64	0.36	9.49	6.32	-	0.85
	M4X6(not analysed)	-								1.28
	M4X5 total	93.8	85.0	6.17	1.40	0.59	2.94	-	3.9	0.87
	Dist.fr. < 205°C	6.36	86.2	7.87	0.84	0.62	4.47	7.69	-	1.10
	205 - 275°C	1.24	89.0	7.52	1.00	0.40	2.08	2.96	-	1.01
	275 - 300°C	5.65	89.7	6.87	1.32	0.31	1.80	3.15	-	0.92
	300 - 400°C	54.65	90.0	6.26	0.87	0.64	2.23	2.19	-	0.83
	400 - 450°C	7.41	89.4	6.19	2.05	0.42	1.94	3.21	-	0.83
	Residue 450+	18.49	65.9	5.22	1.10	0.56	7.43	n.d.	19.79	0.95
7.	Feed		80.2	5.82	1.07	0.67	7.64	n.d.	4.6	0.87
	M3X3(organic phase)	1.1	87.8	9.57	0.68	0.36	1.59	3.91	-	1.31
	M4X6(not analysed)	2.7								0.93
	M4X5 total	91.1	83.8	6.04	0.88	0.66	3.92	n.d.	4.7	0.86
	Dist.fr. < 205°C	1.53	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	1.10
	205 - 275°C	3.63	88.8	7.39	0.50	0.31	3.0	4.15	-	1.0
	275 - 350°C	45.58	90.6	6.24	0.43	0.61	2.12	2.70	-	0.83
	350 - 407°C	16.37	91.0	5.87	0.88	0.52	1.73	2.23	-	0.77
	407 - 450°C	3.68	88.2	6.64	1.15	n.d.	4.01	3.90	-	0.90
	Residue 450+	20.32	62.4	3.80	1.19	0.98	3.33	n.d.	28.3	0.73

TABLE 5.8: (continued)

Exp No.	Sample Analysed	% weight of Total Liquid Feed	% wt C	H	N	S	O by diff	O N. Act.	Ash	H/C
8.	Feed	100	83.5	5.79	1.10	0.55	5.86	n.d.	3.2	0.83
	M3X3(not analysed)	0.8								
	M4X6 " "	2.7								
	M4X5 total	92.5	87.4	9.46	0.81	0.59	1.74	n.d.	-	1.30
	Dist.fr. < 205°C	1.0	86.2	6.08	0.98	0.57	2.76	n.d.	3.41	0.85
	205 - 275°C)	39.4	71.4	7.02	0.45	0.28	20.85*	7.34	-	1.18
	275 - 350°C)		89.3	7.28	0.30	0.37	2.75	2.93	-	0.98
	350 - 407°C	22.7	90.1	6.45	0.48	0.51	2.46	2.74	-	0.86
	407 - 450°C	5.0	92.0	5.90	1.06	0.66	0.38	1.68	-	0.77
	Residue 450+	21.0	90.3	5.98	1.10	0.51	2.11	2.95	-	0.79
			68.7	4.55	2.03	0.67	9.23	n.d.	14.82	0.79
9.	Feed (not analysed)	100								
	M3X3 " "	0.3								
	M4X6 " "	4.0								
	M4X5 total	92.2	84.2	5.86	0.91	0.54	4.43	n.d.	4.06	0.84
	Dist.fr. < 205°C	0.7	78.8	6.88	0.32	0.49	13.51*	3.60	-	1.05
	205 - 275°C	5.0	89.4	7.29	0.51	0.56	2.24	2.80	-	0.98
	275 - 350°C	32.1	90.7	6.35	0.57	0.69	1.69	1.70	-	0.84
	350 - 407°C	21.1	91.6	5.57	0.80	0.71	1.32	3.42	-	0.73
	407 - 450°C	9.0	89.6	5.80	1.30	0.57	2.73	n.d.	-	0.78
	Residue 450+	22.8	69.2	3.85	1.78	0.71	7.86	n.d.	16.60	0.67
10.	Feed (not analysed)	100								
	M3X3 " "	2.4								
	M4X6 " "	5.9								
	M4X5 total	85.6	85.3	5.70	0.8	0.53	4.0	n.d.	3.62	0.81
	Dist.fr. < 205°C	1.8	74.0	7.78	0.40	0.35	17.47*	9.76	-	1.26
	205 - 275°C	4.9	89.6	7.12	0.40	0.45	2.43	2.88	-	1.69
	275 - 350°C	35.2	90.6	6.18	0.59	0.62	2.01	2.61	-	0.95
	350 - 407°C	15.2	91.7	5.58	0.90	0.53	1.29	1.85	-	0.73
	407 - 450°C	4.5	88.8	5.89	1.35	0.57	3.39	4.76	-	0.79
	Residue 450+	22.01	70.9	4.04	1.63	0.62	6.11	n.d.	16.7	0.68

SBRAG

TABLE 5.8:(continued)

Exp No.	Sample Analysed	% weight of Total Liquid Feed	% wt C	H	N	S	O by diff	O N. Act.	Ash	H/C
11.	Feed (not analysed)	100								
	M3X3 " "	0.9								
	M4X6 " "	4.2								
	M4X5 total	85.4	85.6	6.05	0.96	0.56	4.35	n.d.	2.48	0.85
	Dist.fr. < 205°C	2.9	58.6	3.74	0.06	0.31	37.29*	n.d.	-	0.77
	205 - 275°C	7.4	89.7	6.70	0.40	0.43	2.77	2.87	-	0.89
	275 - 350°C	35.0	91.2	6.33	0.45	0.60	1.42	2.57	-	0.83
	350 - 407°C	14.8	90.8	5.74	0.91	0.52	2.03	2.12	-	0.76
	407 - 450°C	3.2	89.7	6.10	1.48	n.d.	n.d.	n.d.	-	0.82
	Residue 450+	22.1	75.2	4.58	2.00	0.61	1.41	n.d.	16.2	0.73

Notes:

n.d. = not done
- = nil
* these results are probably invalidated by the loss of volatile compounds during the analysis

amount of fresh coal added to each slurry batch varied from pass to pass being a function of the solids content of the solvent recycled and was calculated on the basis of maintaining the THF insoluble content of the resulting slurry feed at 35% wt.

The notion of "pass" was adopted for the purpose of being able to follow the change in the quality of feed and products in the evolution of the conversion and yields. A pass was defined as the part of the run corresponding to the period when one batch of slurry feed was pumped into the unit. Since each slurry batch was a combination of fractions of product obtained in the previous so called "pass" one can simulate a "pass" with the passage through the reactor of a specific feed and regard the run as a succession of tests. The average duration of a pass was seven hours corresponding to about seven reactor volumes. The composition of the solvent varied from pass to pass both in solids content and in the composition of the liquid phase.

Data collected over period of 3 to 7 hours during which all operation parameters including feed composition were constant provided basis for material balances, conversion and yields calculation at intervals during each run. The results will be discussed in this report.

The various solids separation methods produced significantly different results, yielding important conclusions and some valuable lessons which helped to shape our process development criteria for both primary liquefaction and product recovery.

5.5.1 RECYCLE SOLVENT RECOVERED BY VACUUM FILTRATION

The operating conditions were 425°C reactor temperature and 24.2 MPa pressure in the system, retention time in the reactor around 60 minutes gas flow 1200 L/h (± 100 L/h). Feedstock used was the Saskatchewan lignite described in Tables 5.4 and 5.5 and pure hydrogen. The solids recovery method was vacuum filtration (without filter aid). The start-up solvent used for this run was the Wilsonville solvent described in Table 5.6.

Table 5.9 shows the detailed operating conditions for each pass and the results: conversion, liquid, gas and water yields and the hydrogen consumption.

The conversions and yields calculated on the basis of total insoluble organic matter entering each pass (without differentiation between fresh coal feed and recirculated organic solids present in the solvent) are in the same range (73-83% wt.) as the values obtained in the once-through tests conducted with anthracene oil at similar conditions. The apparent scattering results was probably caused by the overlapping of the passes due to the lack of experience in conducting recycle runs which, combined with the increasing difficulties in the filtration of the heavy product, resulted in small slurry batches (shorter passes). Thus the short duration of passes did not allow for neat separation and representative sampling. The data is presented in

TABLE 5.9: RUN NO. 8 RESULTS (SOLIDS REMOVED BY FILTRATION)

PASS #	1	2	3	4	5	6	7	8	9	10
LHSV (h^{-1})	.990	1.032	.962	.973	.979	1.016	1.026	.928	.853	.958
G/L (L/kg)	165	145	197	196	198	188	186	205	204	230
Conversion % maf	83.5	83.0	77.4	86.9	77.7	73.6	75.3	82.9	82.1	64.1
Liquid yield "	62.7	63.9	56.3	71.0	60.9	51.9	52.1	66.3	56.6	37.4
H_2 cons. "	1.9	1.4	4.0	3.1	3.1	2.4	3.0	3.1	2.7	2.1
H_2O make "	9.2	2.6	2.7	1.9	4.1	6.1	6.5	2.9	1.9	12.7
CO CO_2 "	3.8	8.3	9.9	7.3	7.1	8.7	9.3	7.1	9.0	7.0
C_1-C_3 "	6.6	7.7	11.6	9.6	8.2	8.9	7.5	9.5	16.9	8.5
H_2S "	1.1	1.0	.9	.3	.4	.4	.3	.3	.5	0.3
Conversion from fresh coal % maf	83.5	87.3	80.0	93.4	82.8	82.8	89.3	92.3	91.9	89.1
Liquid from fresh coal % maf	62.7	68.7	59.2	78.8	67.5	62.2	66.8	77.3	66.4	61.3
Mass balance % measured	96.7	95.1	101.3	99.5	98.8	95.1	94.4	104	112.7	100.7

graphic form in Fig. 5.5 and 5.6. Considering that the recirculated organic solids are at least in part inertinitic in nature, the data suggests an improvement in conversion with the recirculation of solids. This is (probably) mostly due to the concentration of condensed polycyclic components which are better solvents for the coal (see Table 5.10 and Figure 5.7). This beneficial effect was found to be limited probably by the loss of hydrogen donor capability of the solvent. The Table 5.10 presents the evolution of the solids free liquid composition (shown as oils, asphaltenes and preasphaltenes content) in feed and product for the 10 passes completed in Run 8. It appears from the data presented in this Table that at a reaction temperature of 425°C and where filtration is used for solids removal and the solvent is not hydrogenated prior to reuse, the cyclohexane insoluble portion of the liquid (asphaltene and preasphaltene) increases with the number of passes. This accumulation was also observed in the physical appearance of the product which became stickier and more viscous.

The filtration rate and performance (measured as solids removal) decreased in relation with the increase in asphaltene and preasphaltene content of the reactor output, with the solids content (THF insoluble) and probably reduction in particle size. It is assumed that the increase in the solvent viscosity caused considerable fluid dynamic changes inside the reactor resulting in poor mixing and mass and heat transfer and consequently in a drop in the conversion and liquid yield observed in the tenth pass. (Conversion dropped from 80% average for passes 4-9 to 64% in pass 10 and the liquid yield from 59.6% average for passes 4-9 to 37.4% in pass 10.)

The deoxygenation data (yield of H_2O, CO and CO_2 as shown in Fig. 5.6) indicate that on an average 47% of the oxygen present in the feed (between 6.8 and 12.4% of maf) was removed as water and carbon dioxides. The products have an overall oxygen content of 3-7%, which indicates that they will require upgrading treatment.

In the lower section of Table 5.9 are presented the conversion and liquid yields data calculated on the basis of fresh coal only (the method of calculation was described in section 5.2.3). The conversion averages 87.5% for the pases 2-9 indicating a definite improvement with the recycle. Likewise the liquid yield averages 68.4% with peaks at 77.3% and 77.8%. Such a liquid yield translates in a potentially gross yield of 4.4 barrels/tonne maf coal (or 3.65 barrels/tonne of lignite) before upgrading. This result must be regarded with caution, as the amount of fresh coal added to the feed in the latter passes was relatively small and the force effect of the fresh coal may have been influenced by this factor.

5.5.2 RECYCLE SOLVENT RECOVERY BY VACUUM DISTILLATION

The objective of this run was to assess the stability of the whole system when the recycle solvent was obtained through vacuum distillation. The operating conditions for this run were: reactor pressure and temperature 24.2 MPa and 440°C respectively, retention time at the reaction temperature 1 hour, the hydrogen was recirculated at flow average 1175 L/hr (1115-1203

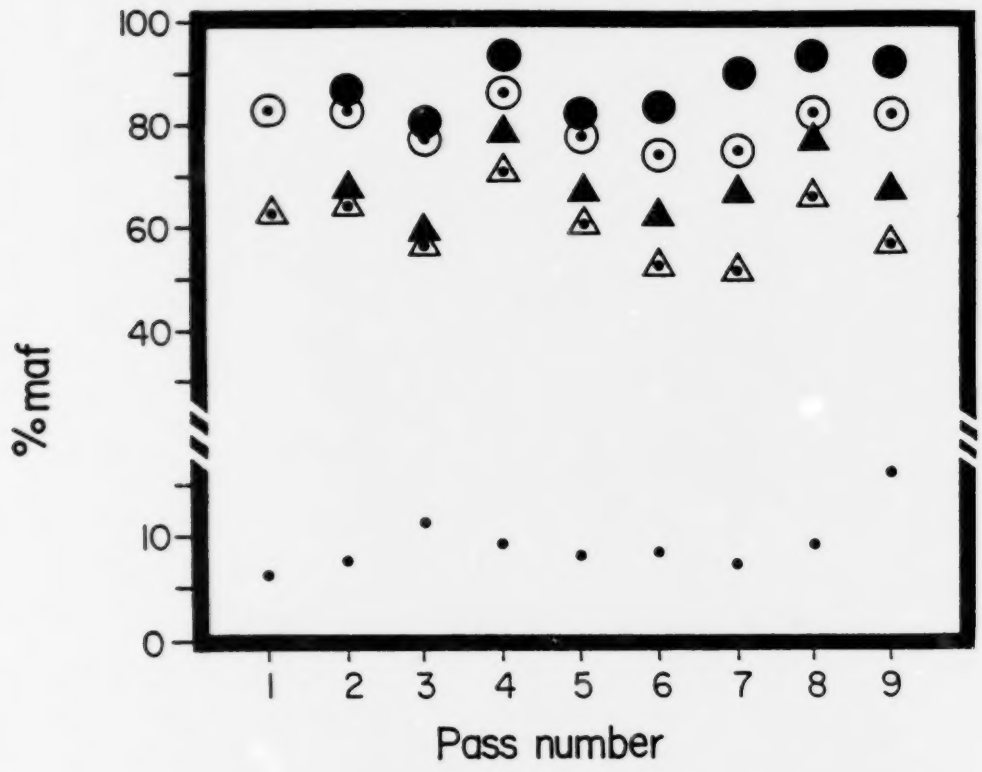


Fig 5.5 Evolution of conversion, liquid yield and gas yield with the number of passes Recycle solvent via vacuum filtration

⊙	CONVERSION	BASIS TOTAL MAF
●	CONVERSION	BASIS MAF FRESH COAL
△	LIQUID YIELD	BASIS TOTAL MAF
▲	LIQUID YIELD	BASIS MAF FRESH COAL
•	GAS YIELD	BASIS TOTAL MAF

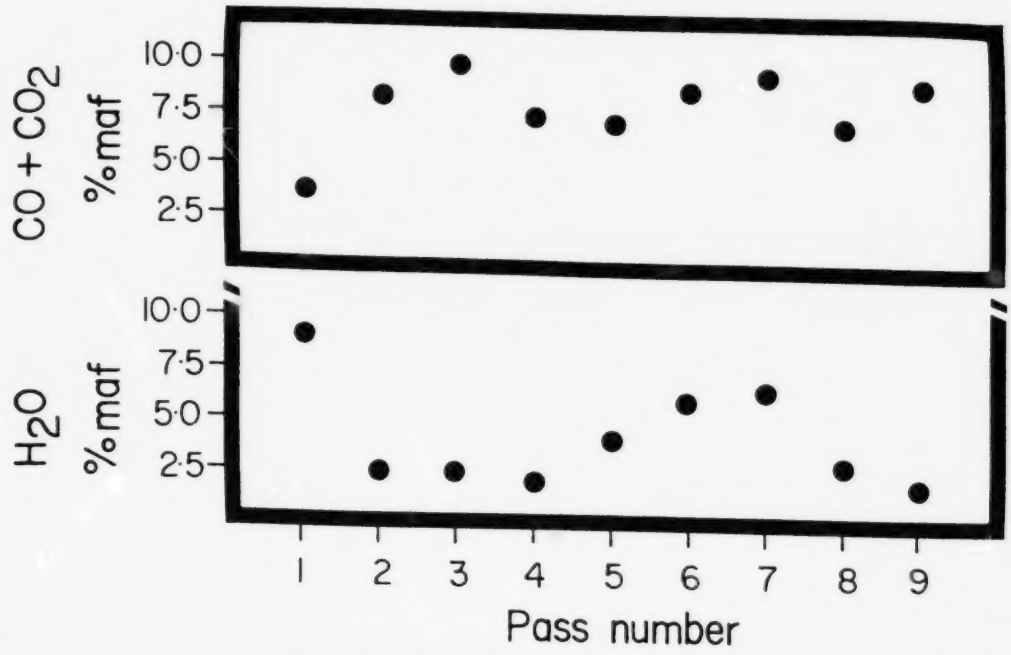


Fig 5.6 Evolution of oxygen removal data with the number of passes Recycle solvent recovered via vacuum filtration

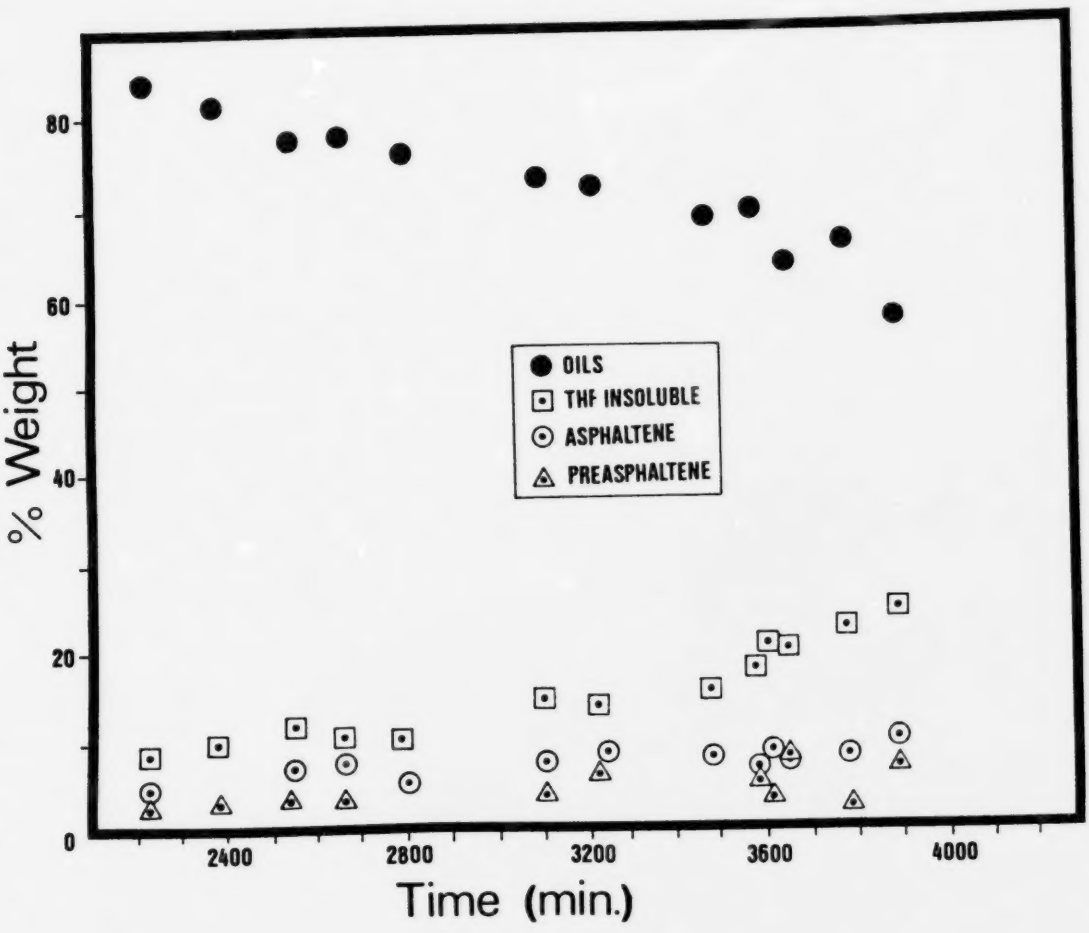


Fig 5.7 Evolution of heavy product composition as a function of time, Run 8

TABLE 5.10: SOLIDS FREE LIQUID COMPOSITION OF HEAVY PRODUCT

Run 8

PASS	Cyclohexane soluble IN	OUT	Asphaltene* IN	OUT	Preasphaltenes* IN	OUT
1	100	91.89	-	5.16	-	2.93
2	n.d.	90.83	n.d.	5.38	n.d.	3.78
3	n.d.	87.64	n.d.	8.17	n.d.	4.18
4	90.25	85.3	5.88	5.98	3.86	8.71
5	89.54	86.37	6.55	8.07	3.89	5.54
6	85.39	85.97	8.95	9.0	5.65	5.01
7	84.83	83.88	9.75	8.82	5.41	7.29
8	82.6	81.6	9.54	10.04	7.85	8.35
9	80.04	80.46	10.86	10.10	9.09	9.46
10	78.34	76.7	11.18	13.8	10.48	9.50

n.d. = not determined
* asphaltene are determined as: cyclohexane insoluble, toluene soluble
preasphaltene are determined as: THF soluble

L/hr). The start-up solvent was anthracene oil (for composition See Table 5.6).

The recycle solvent was a mixture of 250-450°C vacuum distilled cut and of non-distilled non-flashed heavy product (M4X5) recovered from the process. By distilling approximately half of the heavy product and thus removing the asphaltenes and preasphaltenes with the vacuum bottoms, the amount of these materials present in the recycled solvent was lower than in previous runs. The ratio of distilled to non-distilled product and the amount of fresh coal added were not the same for all passes.

The overall results obtained are presented in Table 5.11. It is to be noted that each one of the passes correspond to a timed experiment (typically four hours of material balances) during the run. The overall results are displayed in graphic form in Figures 5.8 to 5.9.

For each pass the conversion values calculated in Run 10 are considerably higher than the ones calculated in Run 8. The conversion and yields in the first pass are slightly higher when compared to the once-through experiments conducted with anthracene oil. This is probably due to higher temperature (440°C in Run 10).

The conversion values are 88-95% maf obtained in the subsequent passes indicate that the recycle of a limited amount of insolubles has a beneficial effect on the coal conversion. Also it appears that the recycle coal-derived solvent obtained through this method is a better solvent in this process. Relatively good liquid yields were obtained all the way through the 10 passes. Yields of 12-15% for H_2O, 5% C_1-C_3 and 10% for CO, CO_2 resulted.

The operation was quite stable and no problems were encountered during the run of over 70 hours.

The overall conversion and liquid yields refer to the total input of THF insoluble organic matter to the reactor regardless of whether it comes from fresh coal or from the recycle solvent. While the yield per pass from total insoluble organic matter is of interest, the significant product yield in a steady-state, commercial application is the yield per unit of fresh coal feed.

Conversion and liquid yields obtained from fresh coal only and per pass can be calculated under the same limiting assumptions as done for Run 8.

Table 5.11 shows conversion and liquid yields from fresh coal only, as compared to overall conversions and liquid yields. The differences are not as great as expected in view of the low amount of IOR recycle and the little changes observed in the recycle solvent itself during the second pass. This is an important observation since it suggests that the chosen operational conditions for recycling lead to a rather stable overall operation. Also hydrocracking of the recycle solvent is limited under the conditions used.

TABLE 5.11: RUN NO. 10 RESULTS (SOLIDS REMOVED BY DISTILLATION)

PASS #	1	2	3	4	5	6	7	8	9	10
LHSV (h^{-1})	.997	.912	1.013	1.000	.960	1.006	.979	1.027	.989	.977
G/L (L/kg)	220	230	190	180	197	192	186	174	190	192
Conversion % maf	84.9	91.0	88.0	91.3	91.9	95.7	93.4	89.6	91.8	87.6
Liquid yield "	63.5	67.6	72.9	66.4	61.3	64.5	72.9	60.5	68.6	63.3
H2 cons. "	5.1	3.3	2.7	1.3	1.2	2.0	2.3	.9	1.5	2.0
H2O make "	11.0	12.4	5.0	9.4	13.6	18.1	12.0	13.5	8.2	12.7
CO CO2 "	11.4	9.3	8.6	10.3	12.1	10.2	8.0	10.3	10.4	9.2
C1-C3 "	3.7	4.6	3.8	6.1	5.9	4.5	2.5	5.9	5.6	4.1
H2S "	.4	.4	.3	.3	.4	.3	.3	.3	.3	.3
Conversion from fresh coal % maf	84.9	93.6	89.7	94.0	93.8	97.2	96.1	93.1	96.5	88.7
Liquid yield " from fresh coal	63.5	70.3	75.0	69.2	63.1	66.0	75.8	63.8	73.5	64.4
Mass balance %	100.8	97.0	96.7	98.3	96.4	98.9	98.0	95.2	100.0	96.7

SBRC

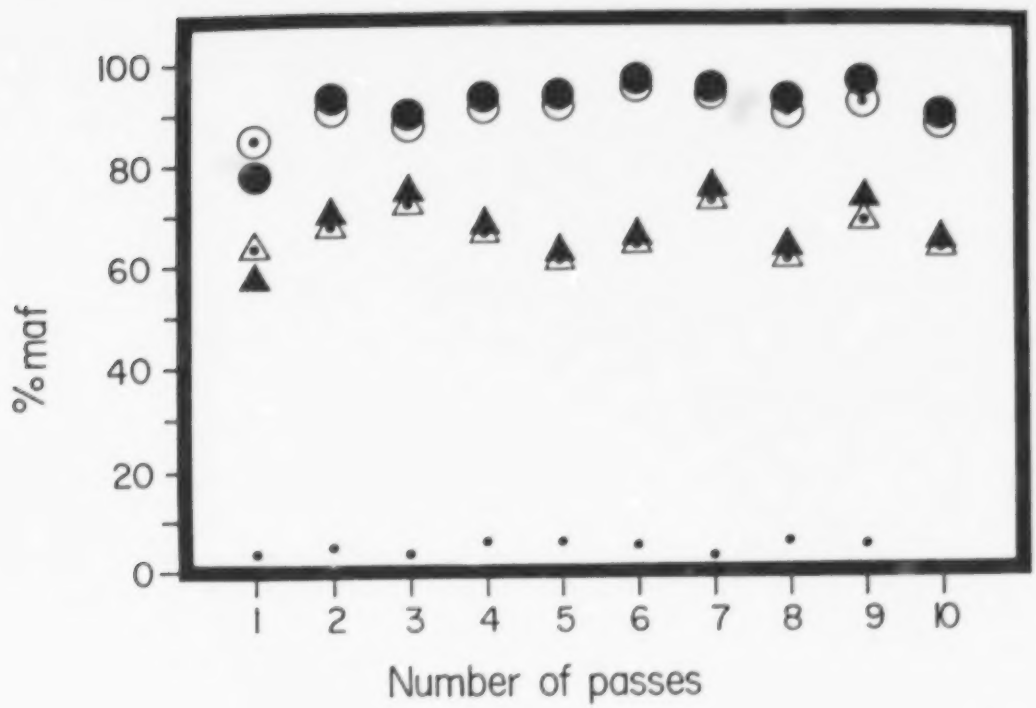


Fig 5.8 **Evolution of conversion, liquid yield and gas yield with the number of passes Recycle solvent recovery via vacuum distillation**

⊙	CONVERSION	BASIS TOTAL MAF
●	CONVERSION	BASIS MAF FRESH COAL
△	LIQUID YIELD	BASIS TOTAL MAF
▲	LIQUID YIELD	BASIS MAF FRESH COAL
•	GAS YIELD	BASIS TOTAL MAF

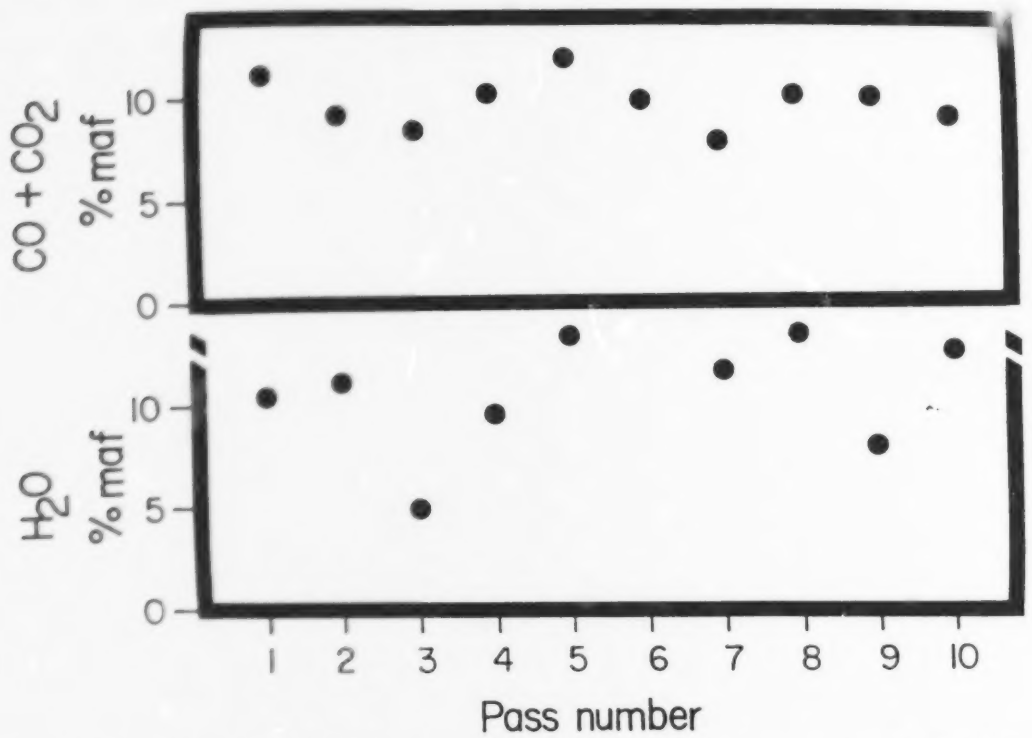


Fig 5.9 Evolution of oxygen removal data with the number of passes Recycle solvent recovery via vacuum distillation

From Figure 5.8 it appears that the stability of the recycle run was quickly achieved in terms of the consistency of product quality. Large differences appear however in the H_2O formation during the run as shown in Figure 5.9 where the net yields of H_2O and CO, CO_2 are plotted as a function of the number of passes. Difficult H_2O measurements due mainly to azeotrope formation may account for the large scattering observed. It is to be noted that deoxygenation will correspond to the quantitative estimates which can be made from this graph since all the oxygen removed from the coal must appear either as H_2O or CO, CO_2.

The quality of the products obtained is shown in Figure 5.10 where the overall liquid yields are presented in terms of cyclohexane solubles (closely related to distillables), asphaltenes and preasphaltenes.

It should be underlined however that these are gross yields and that depending upon the solids separation method employed for recovery of liquid products, the net yield of a plant will be a function of the efficiency of the liquid recovery process.

Figure 5.11 and Table 5.12 show evolution and heavy product composition during the run. An important feature of the figure is that the oil content steadily decreases while there is a steady increase of asphaltenes, preasphaltenes and THF insolubles (ash and IOR). Under these conditions the operation of the liquefaction unit continued to be completely satisfactory.

Table 5.13 shows the elemental composition of the derived liquids and their H/C atomic ratio. In all cases the H/C ratio is still low after primary liquefaction, little denitrogenation takes place and the O,S content remains very high. Since the initial sulfur content of the lignite used is 1.3% wt maf coal and the H_2S formed varies between 0.3 and 0.4% wt maf coals, we must conclude that a significant quantity of organic sulfur in the order of 20 to 30% is removed during primary liquefaction.

In conclusion, Run 10 has shown the feasibility of the recycle operation using vacuum distillation of the primary liquefaction products. A stable operation was rapidly achieved after three to four passes judging from the H_2 consumption data. Extensive H_2O production is a mark of the reaction with the highly oxygenated lignite. The liquid product contains a substantial amount of cyclohexane soluble matter (a measure of distillables) yet it still contains N, S and O in quantities which will require extensive upgrading. The overall recycle operation requires a control of the levels of asphaltenes, preasphaltenes and THF insolubles (ash plus inertinitic organic material).

5.5.3 RECYCLE SOLVENT RECOVERY BY CENTRIFUGATION

This recycle run was conducted under conditions such that the recycle material was obtained through centrifugation as described in the experimental section.

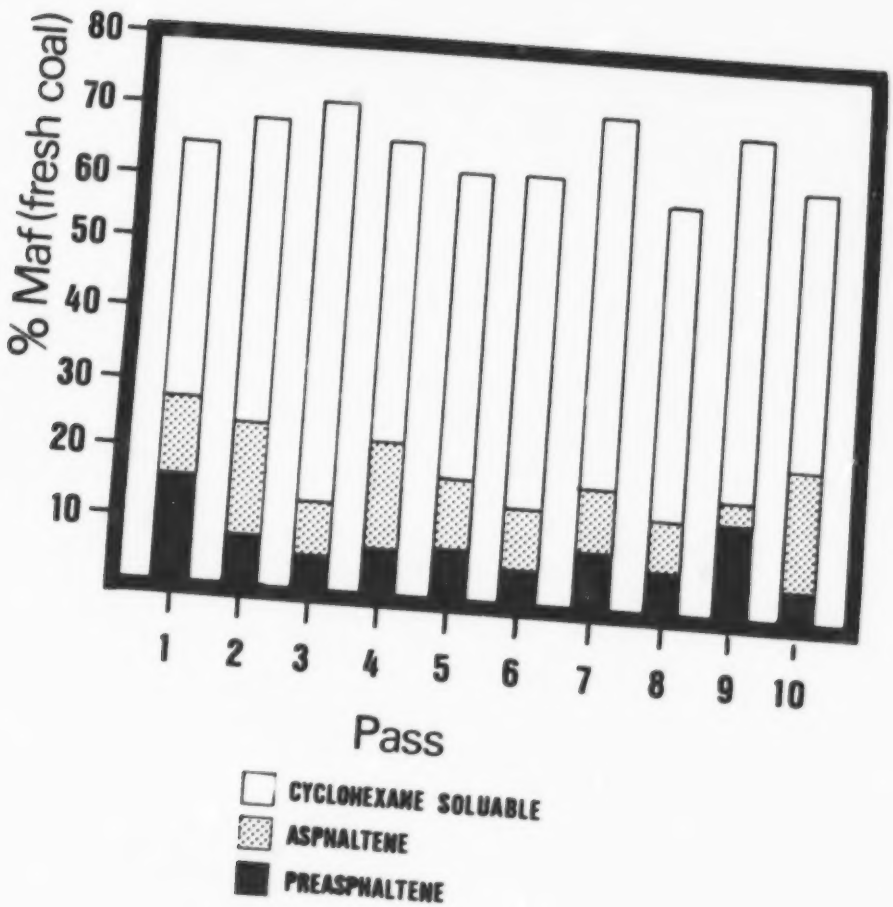


Fig 5.10 Run 10 Product Yields

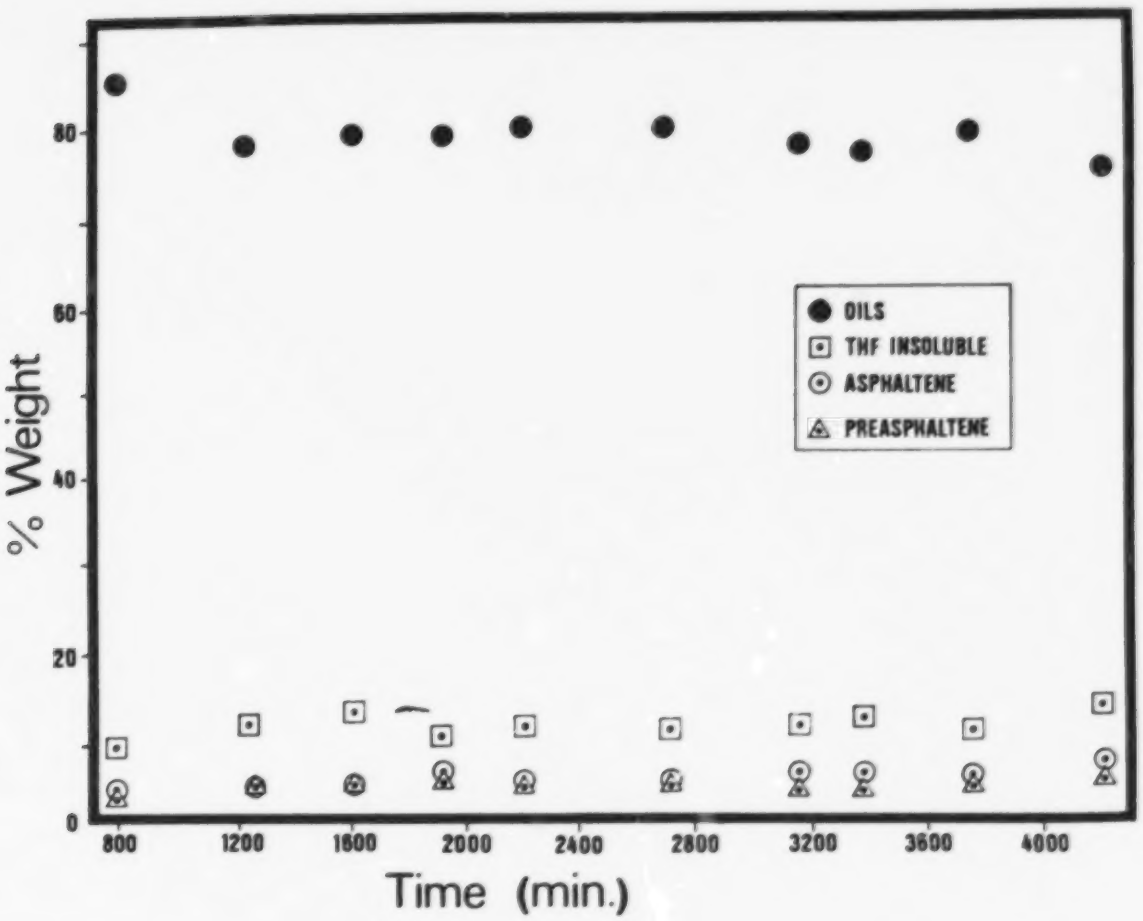


Fig 5.11 Evolution of heavy product composition as a function of time, Run 10

TABLE 5.12: SOLID FREE LIQUID COMPOSITION OF TOTAL LIQUID REACTOR PRODUCT RUN 10

PASS	Cyclohexane Soluble		Asphaltene		Preasphaltene	
	IN	OUT	IN	OUT	IN	OUT
1	100	92.3	-	3.3	-	4.4
2	96.3	88.7	1.5	6.95	2.1	4.35
3	94.5	91.2	3.3	5.36	2.0	3.4
4	97.11	89.8	1.7	6.4	1.2	3.8
5	96.45	90.4	2.2	5.4	1.2	4.2
6	95.4	91.4	2.6	5.3	2.0	3.3
7	95.6	88.2	2.7	7.3	1.7	4.5
8	93.8	89.9	3.8	6.1	2.3	4.0
9	94.4	89.6	3.4	3.8	2.2	6.6
10	94.2	87.3	2.1	8.3	3.7	4.4

TABLE 5.13: ELEMENTAL ANALYSIS (C,H,N,) OF THE HEAVY PRODUCT DURING RECYCLE RUN 10

PASS	N	C	H	Atomic H/C ratio
1	1.3	82.7	6.0	0.87
2	1.1	81.7	6.1	0.90
3	1.5	82.0	6.4	0.94
4	1.4	81.0	6.2	0.92
5	1.1	79.1	6.0	0.91
6	1.1	80.1	6.2	0.93
7	1.1	78.1	6.3	0.97
8	1.2	76.0	6.7	1.06
9	1.4	84.1	6.3	0.90
10	1.2	75.8	6.3	1.00
m.a.f. coal	2.1	72.3	5.0	0.83

Seven passes corresponding to seven recycles were conducted with fresh coal additions at each pass. The centrifuge operation data is shown in Tables 5.14 and 5.15 and Figure 5.16.

The characteristics of the heavy product varied with each pass with the gravity, viscosity and solids content increasing. This made the centrifugation more difficult as the overflow stream became stickier until the viscosity of the slurry made it arduous to operate beyond pass 7. A decision was made to hydrocrack the recycle material under the same experimental conditions (pass 8) and in the presence of red mud (iron oxides mixture coming from alumina smelting operations) during pass 9. Results and discussion of these last two passes are presented in a separate section of the report.

Table 5.16 shows the overall results obtained together with the results (conversion and liquid yields) derived from the data assuming that the recycle solvent behaves identically to the solvent hydrocracked in pass No. 8. The data of Table 5.16 is presented in graphical form in Figures 5.12 and 5.13. Similar patterns are observed for overall conversion and liquid yields. It should be noted that the LHSV was increased during the run due to mechanical problems related to operation of the high pressure feed pump.

The quality of the product stream has been followed in terms of oils (cyclohexane solubles), asphaltenes (toluene solubles) and preasphaltenes. Figure 5.12 and Table 5.17 show the evolution of the different components of the slurry collected in the first receiver (M3X1) as a function of run time. Clearly a trend towards stability of the composition is reached after pass 5.

Using the same assumption as for the runs No. 8 and 10, (that the organic insoluble material recycled into the system will behave similarly to pass 8 where no fresh coal is added), the conversion, liquid yield and composition (oils, asphaltene, preasphaltene) of the product were calculated for fresh coal and recycle insoluble maf material.

Figure 5.15 shows the distribution of the net product in terms of oils, asphaltenes and preasphaltenes derived from fresh coal and from recycle material. It is important to note that a net production of oils is obtained from the recycle asphaltenes and preasphaltenes. Conversly asphaltenes and preasphaltenes show a net consumption.

In conclusion, the operation during this recycle run was affected by the accumulation of heavy material (asphaltenes and preasphaltenes). The viscosity of the slurry increased substantially and only seven complete recycle passes were attained. Liquid yields were high although the eventual recovery of oils from the overall mixture was not attempted and might be limited by fluid dynamic considerations as in Run 8.

TABLE 5.14: RECYCLE RUN NO. 11 - CENTRIFUGE OPERATION

Centrif. No.	Feed produced	Overflow used	Centrifuge Feed			Separated Streams				Centrifuge effectiveness solids removed x100% / solids feed
			Kg	% THF insoluble	Gravity	Overflow kg	Overflow % THF insol	Cake kg	Cake Average THF insol	
1	1	2	10.94	8.7	1.153	8.49	0.47	2.31	37.2	95.8
2	2	3	19.96	10.83	1.173	16.05	0.22	3.56	54.7	98.4
3	3	4	20.09	13.47	1.188	15.25	1.80	4.24	50.5	89.9
4	4	5	20.82	15.24	1.161	16.78	5.30	4.20	56.3	71.9
5	5	6	30.37	18.33	1.179	24.86	12.40	4.48	44.9	44.5
6	6	7	18.86	21.65	1.185	15.06	15.10	3.01	47.4	44.2

TABLE 5.15: RECYCLE RUN No. 11 - CENTRIFUGE PERFORMANCE

Centri-fugation #	Feed Compositon %							Overflow Liquid Composition %						
	Suspension				Solids Free Liquid			Suspension				Solids Free Liquid		
	O	A	PA	S	O	A	PA	O	A	PA	S	O	A	PA
1				8.7				91.3	4.3	3.9	0.49	91.7	4.3	3.4
2	79.3	4.0	5.9	10.8	88.9	4.5	6.6	91.6	4.3	3.9	0.22	91.8	4.3	3.9
3	76.9	4.0	5.6	13.5	88.9	4.6	6.5	86.4	5.1	6.7	1.80	88.0	5.2	6.8
4	71.3	4.9	8.6	15.2	84.1	5.8	10.1	83.5	3.4	7.8	5.3	88.2	3.6	8.2
5	66.2	4.9	10.6	18.3	81.0	6.0	13.0	72.5	6.6	8.5	12.4	82.8	7.5	9.7
6	63.5	5.7	9.2	21.6	81.0	7.3	11.8	68.0	7.1	9.8	15.1	80.1	8.4	11.5

Notes: O = oils
A = asphaltenes
PA = preasphaltenes
S = solids (THF insolubles)

TABLE 5.16: RUN NO. 11 RESULTS (SOLIDS REMOVED BY CENTRIGUATION)

PASS #	1	2	3	4	5	6	7
LHSV (h^{-1})	.724	.905	.924	1.037	1.008	1.027	1.082
G/L (L/kg)	166.3	210.8	226.0	195.0	179.0	178.0	200.3
Conversion % maf	82.8	81.3	81.4	77.1	75.1	70.3	62.6
Liquid yield "	59.0	61.6	54.9	55.3	53.4	42.5	42.0
H2 cons. "	2.8	3.9	3.5	2.6	2.4	2.8	2.7
H_2O make "	15.2	7.2	12.2	8.4	8.9	10.7	6.5
CO CO_2 "	5.9	9.4	9.7	7.8	7.9	10.0	10.1
C_1-C_3 "	5.4	6.8	7.8	7.9	7.0	8.7	6.8
H_2S "	.1	.2	.3	.2	.2	1.1	.4
Conversion from fresh coal % maf	82.8	88.4	93.7	93.4	91.5	94.2	72.6
Liquid yield from fresh coal % maf	59.0	69.6	67.0	73.2	71.3	64.6	54.0
Mass balance measured % input	106.1	98.7	102.0	103.7	98.5	100.4	99.4

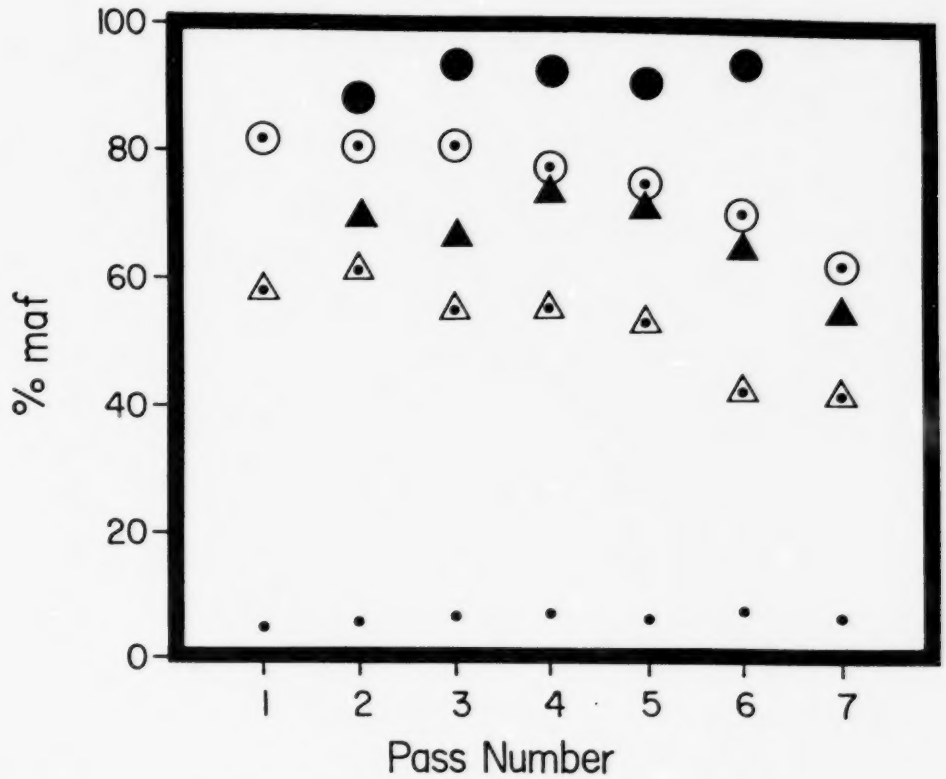


Fig 5.12 Evolution of conversion, liquid yield and gas yield with the number of passes Recycle solvent recovered via centrifugation

⊙	CONVERSION	BASIS TOTAL MAF
●	CONVERSION	BASIS MAF FRESH COAL
△	LIQUID YIELD	BASIS TOTAL MAF
▲	LIQUID YIELD	BASIS MAF FRESH COAL
•	GAS YIELD	BASIS TOTAL MAF

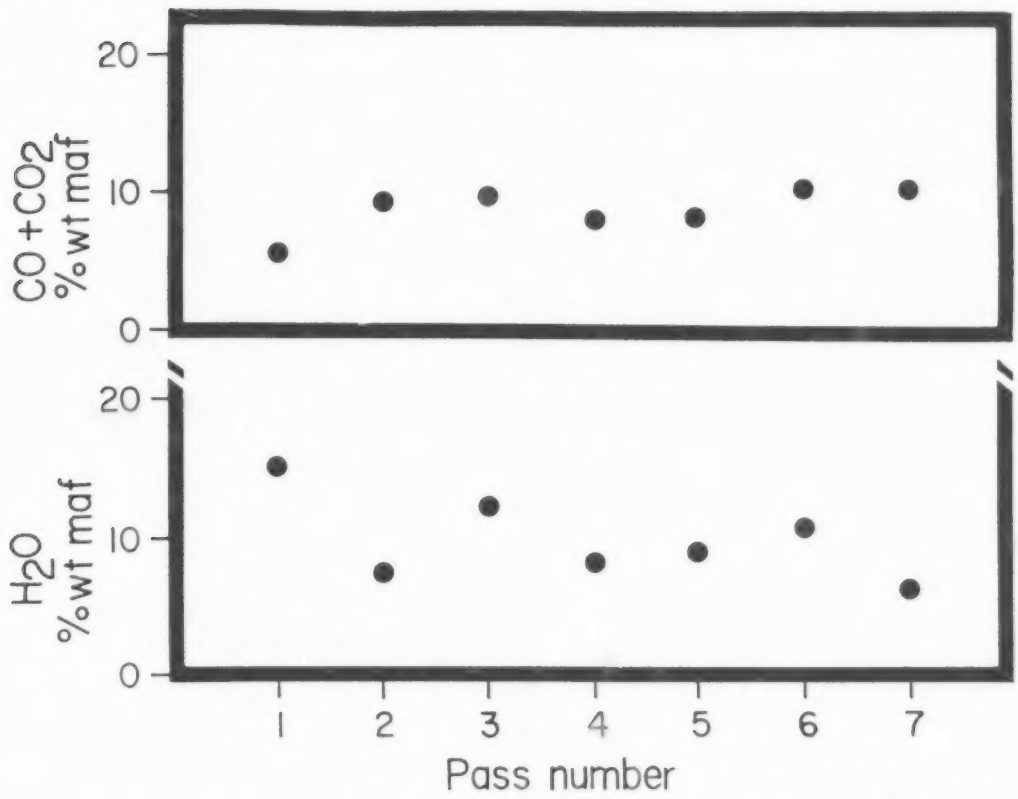


Fig 5.13 Evolution of oxygen removal data with the number of passes Recycle solvent recovered via centrifugation

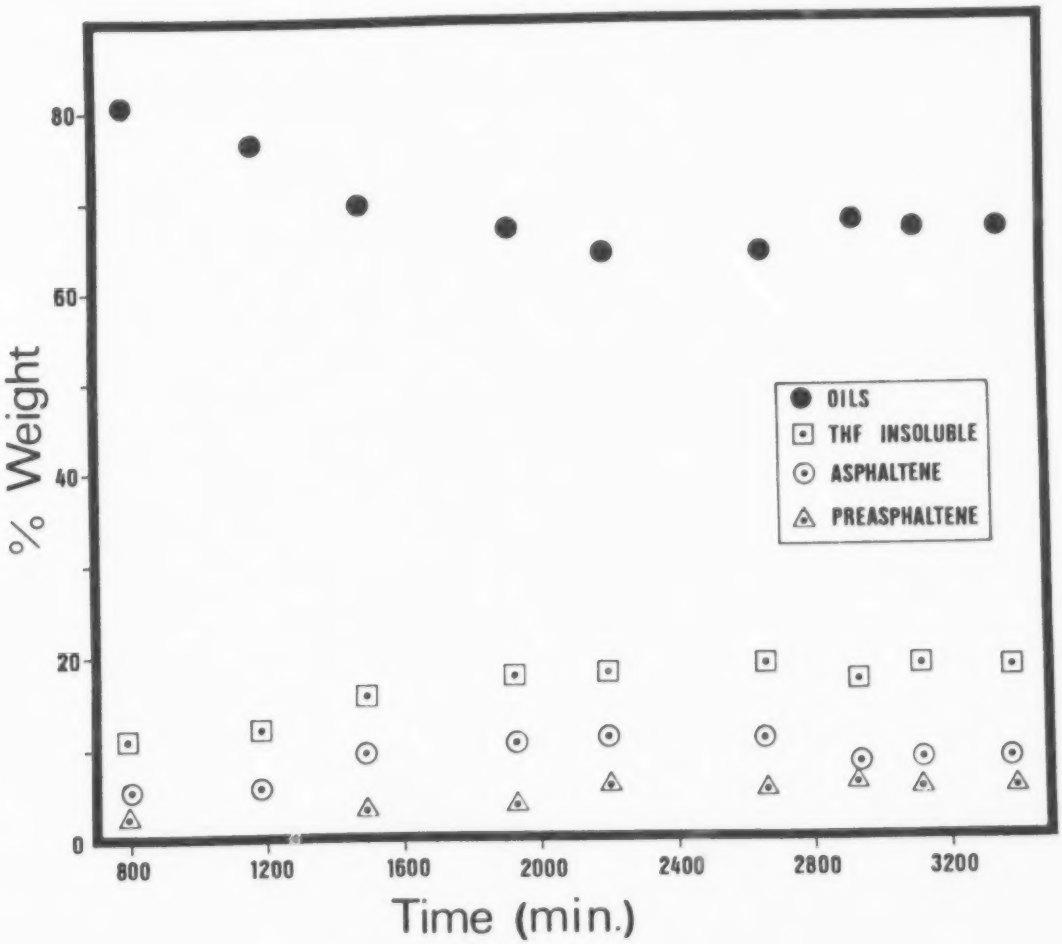


Fig 5.14 Evolution of heavy product composition as a function of time, Run II

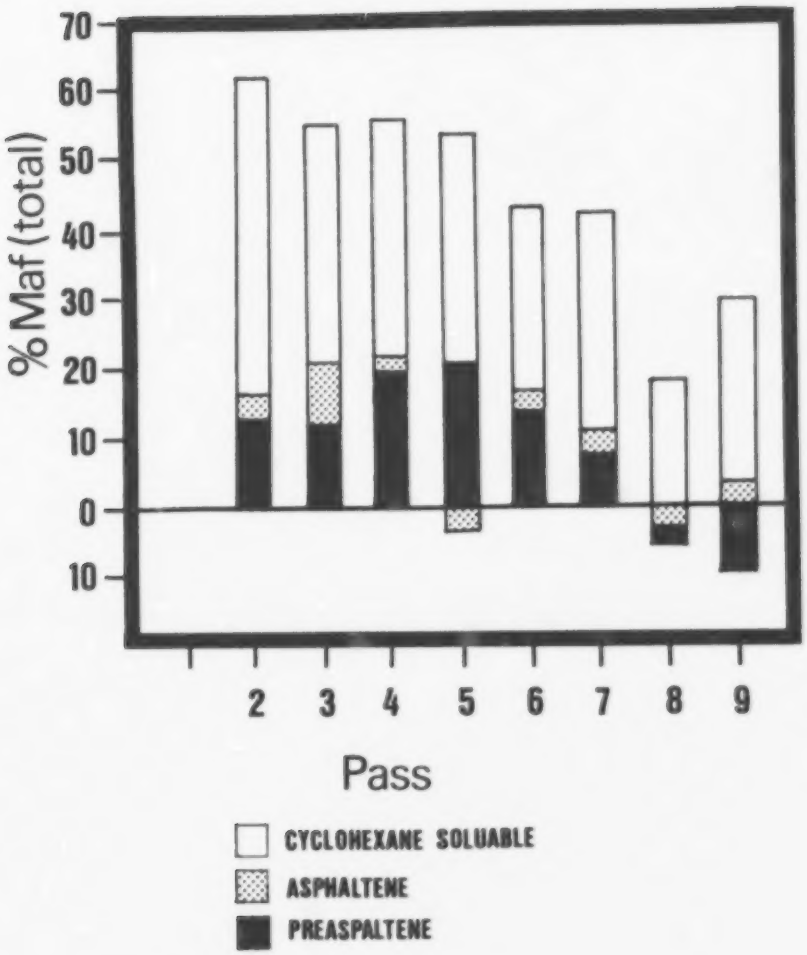
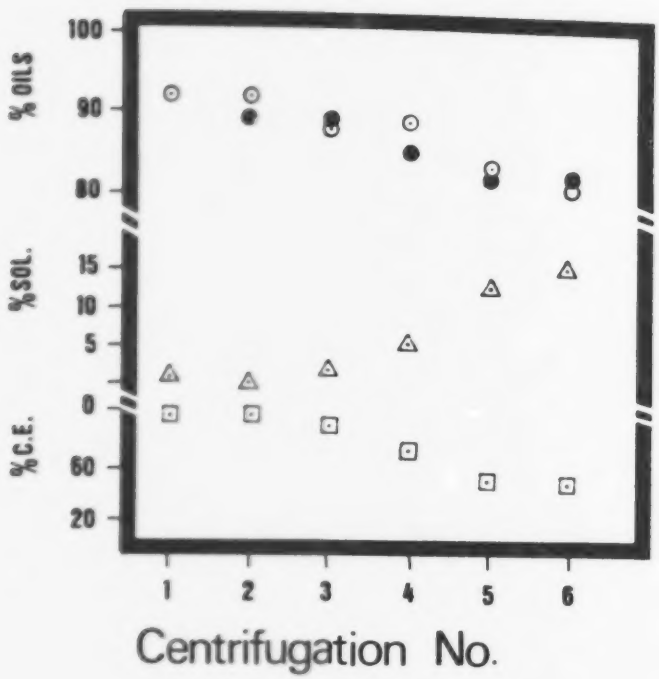


Fig 5.15 Product Yields Run No. 11



● IN FEED ON A SOLIDS FREE BASIS
⊙ CENTRIFUGED LIQUID
△ CENTRIFUGED LIQUID
⊡ CENTRIFUGE EFFECTIVENESS
= (SOLIDS REMOVED/SOLIDS IN FEED) X 100

Fig 5.16 Centrifuge Operation

Run No.11

TABLE 5.17: RUN 11 EVOLUTION OF SOLIDS FREE M3X1 AND FEED COMPOSITION (% WT)

PASS No.	OILS		ASPHALTENES		PREASPHALTENES	
	Feed	M3X1	Feed	M3X1	Feed	M3X1
1	100		-		-	
2	94.6	90.7	2.3	2.9	3.1	6.4
3	93.2	86.49	3.8	6.5	3.0	7.0
4	87.4	81.2	7.3	6.3	5.3	12.5
5	85.5	80.8	8.4	5.2	6.1	14.05
6	81.3	78.0	7.8	7.6	10.9	14.4
7	79.9	79.2	6.9	6.9	13.2	13.9

5.5.4 SOLVENT RECYCLE RUNS - CONCLUSIONS AND RECOMMENDATIONS

The three experimental runs conducted recycling a fraction of product as solvent demonstrated that lignite conversion in integrated system is possible. The conversions are higher than those obtained in the once-through mode and the liquid yields obtained (4.4 bbl/t coal maf) are as high as those obtained in any other known process. The quality of the product obtained in this first step requires improvement by catalytic upgrading.

Neither vacuum filtration nor simple centrifugation of the product resulted in satisfactory solids separation beyond the third pass. This was probably due to increased viscosity (as a result of the increase in concentration of asphaltene - preasphaltene compounds), similarity of gravity and decrease of particle size. The continuous quality changes in the solvent used, especially in Runs No. 8 and 11 interfered with the achievement of steady state even after 7 passes through the reactor.

Run 10 in which the solids removal method employed was vacuum distillation gave trouble-free operation as the data shows achievement of stable operation after pass 4, and high conversions and liquid yield. Such a result suggests that keeping the asphaltene plus preasphaltene content below a certain level (believed to be about 20%) ensures operational viability. In other words, the use of a coal derived solvent containing some asphaltene-preasphaltene appears to be beneficial to the conversion of lignite, but somewhere in the process asphaltene-preasphaltene rich fractions must be removed from the solvent at the rate they are produced in order to avoid build-up of these components. Increasing asphaltene-preasphaltene concentrations lead to increase of viscosity and gravity of the products which interferes with solids separation and result in lower conversion and liquid yields.

Table 5.18 and 5.19 illustrate the progressive change in composition of the liquid feed product, respectively, for each of the three recycle modes used. It is quite clear from the input/output analysis that the distillation run allows a much simpler and lower severity operation by maintaining the asphaltene and preasphaltene content lower than about 6% wt of total liquid feed as recycle solvent to the primary liquefaction reactor. This results in easier control of the fluidity of the coal-solvent slurry and permits keeping the combined asphaltene and preasphaltene levels to less than about 12% as measured in the first receiver. During the filtration and centrifugation runs the combined asphaltene and preasphaltene content reached levels considerably higher than this and caused difficulties in the later passes.

In a recycle operation using lignite as feedstock and a solvent fraction similar to the one used in Run 10, the conversion expected can be as high as 95.4% maf fresh coal with a gross liquid yield above 65% (averaged over passes 4-9 in Run 10).

The relatively high yields of H_2O and carbon oxides (CO,CO_2) are the result of oxygen removal. A large proportion of the hydrogen consumed is used for water production. This suggests as one of the objectives of future work the further investigation of syngas use in conjunction with a shift catalyst in order to reduce the consumption of hydrogen and mitigate the

TABLE 5.18: COMPARISON OF REACTOR LIQUID FEED COMPOSITION AS A FUNCTION OF NUMBER OF PASSES FOR THE THREE RECYCLE RUNS

	INPUT								
	RUN 8 (FILTRATION)			RUN 10 (DISTILLATION)			RUN 11 (CENTRIFUGATION)		
							Atomic		
PASS	O	A	PA	O	A	PA	O	A	PA
1	100	-	-	100	-	-	100	-	-
2	n.d.	n.d.	n.d.	96.3	1.6	2.1	94.6	2.3	3.1
3	n.d.	n.d.	n.d.	94.5	3.3	2.0	93.2	3.8	3.0
4	90.3	5.9	3.8	97.1	1.7	1.2	87.4	7.3	5.3
5	89.5	6.6	3.9	96.5	2.2	1.2	85.5	8.4	6.1
6	85.4	8.9	3.9	95.4	2.6	2.0	81.3	7.8	10.9
7	84.8	9.7	5.5	95.6	2.7	1.7	79.9	6.9	13.2
8	82.6	9.5	7.9	93.8	3.8	2.3			
9	80.0	10.9	9.1	94.4	3.4	2.2			
10	-	-	-	94.2	2.1	3.7			

O = Oils = cyclohexane solubles
A = Asphaltenes = Toluene solubles
PA = Preasphaltenes = THF solubles

TABLE 5.19: COMPARISON OF REACTOR LIQUID PRODUCT COMPOSITION AS A FUNCTION OF NUMBER OF PASSES FOR THE THREE RECYCLE RUNS

REACTOR LIQUID PRODUCT (SOLID-FREE)

	RUN 8 (FILTRATION)			RUN 10 (DISTILLATION)			RUN 11 (CENTRIFUGATION)		
							Atomic		
PASS	O	A	PA	O	A	PA	O	A	PA
1	91.9	5.2	2.9	92.3	3.3	4.4	90.7	2.9	6.4
2	90.8	5.4	3.8	88.7	6.9	4.4	86.5	6.5	7.0
3	87.6	8.2	4.2	91.2	5.4	3.4	81.2	6.3	12.5
4	85.3	6.0	8.7	89.8	6.4	3.8	80.8	5.2	14.0
5	86.4	8.1	5.5	90.4	5.4	4.2	78.0	7.6	14.4
6	85.5	9.0	5.5	91.4	5.3	3.3	79.2	6.9	13.9
7	83.9	8.8	7.3	88.2	7.3	4.5	81.8	7.3	10.9
8	81.6	10.0	8.4	89.9	6.1	4.0			
9	80.4	10.1	9.5	89.6	6.4	4.0			
10	-	-	-	87.3	6.4	6.3			

O = Oils = cyclohexane solubles
A = Asphaltenes = Toluene solubles, cyclohexane insoluble
PA = Preasphaltenes = THF solubles, toluene insoluble

problems of water separation and treatment.

The gross liquid yields obtained in Run 10 indicate a production of 4.4 bbl/t maf coal with a potential of between 3.6 and 4 bbl of distillable product. These figures are of course subject to efficiency of the solids separation method selected. The hydrogen consumption including the upgrading steps would reach 24 550 SCF/t maf[7]).

During the period covered by this report, the H_2 consumption, as calculated on the basis of flow and composition of gas input and output streams, varied around 2% with peaks as high as 4%. The accuracy of the H_2 consumption calculations must be improved to make it independent of the gas flow measurements errors. Future work programs should include a task related to improvement of H_2 consumption measurement.

ANALYSIS OF SECONDARY HYDROCRACKING OF COAL DRIVED LIQUIDS

Two experiments were conducted aiming at hydrocracking the recycle solvent; one with a catalyst, (Run 11-Exp 9) and the other without (Run 11-Exp. 8).

In Run 11-Exp. 8 the centrifugated material to be used as recycle solvent and derived from the product of Run 11-Pass 7 was process through the liquefaction reactor under similar conditions as those used in the difficult passes of Run 11.

In Run 11-Exp. 9 the product of Run 11-Exp. 8, somewhat modified by settling and a few hours storage, was subjected to catalytic hydrocracking bypassing it through the reactor using red mud (iron oxides) as a would-be catalyst. A summary of the two runs is presented in Table 5.20.

It should be noted that hydrogen consumption is relatively high in both experiments.

Table 5.20: OPERATING CONDITIONS AND RESULTS OBTAINED IN HYDROCRACKING LIGNITE DERIVED LIQUIDS1)

Exp NO.	18-08	18-09
Catalyst added	none	red mud (Fe_2O_3 10% maf)
G/L (L/kg)	190.6	187.3
LHSV	1.11	1.07
Feed Viscosity at 59°C (min Pa)	4870	1760
Product viscosity at 59°C (min Pa)	1760	1310

% maf		
Conversion	37.5	20.5
Liquid Yield	12.1	18.8
H_2 consumption	3.6	3.1
H_2O yield	6.3	2.3
CO CO_2	12.2	1.5
C_1-C_3	9.9	7.1
cyclohexane soluble	17.7	24.2
asphaltene	(3.0)	2.4
preasphaltene	(2.5)	(7.8)

1) Reactor conditions 440°C, 24.2 MPa

Table 5.21: QUALITY OF OILS DURING HYDROCRACKING OF LIGNITE DERIVED RECYCLE SOLVENT

Exp.		Distribution of Organic Liquid Yields (%wt) Oils	Asphaltenes	Preasphaltenes	THF insol
18-08	Input Material	62.9	6.2	9.0	21.9
	Reactor prod.	67.5	6.0	8.9	17.6
18-09	Input Material	63.2	4.7	9.8	22.3
	Reactor prod.	67.3	5.0	8.6	19.1

Table 5.21 lists the composition of the feed and product solvent during the hydrocracking experiments. In both cases there is a net increase in Oils and a net decrease in THF insolubles but the Asphaltene-PreAsphaltene content is relatively constant. From this it can be concluded that all of the above are relatively equally susceptible to cracking at these conditions and that the THF insoluble organics undergo some liquefaction during successive passes.

In conclusion, these two tests represent only a very preliminary investigation into the product hydrocracking and confirm that better, more active catalysts are required for hydrotreating. This subject should be further investigated in conjunction with solvent quality standards studies.

6.0 EQUIPMENT PERFORMANCE

Close monitoring of equipment was maintained during the first year of PDU operation and records of all equipment repairs and modifications were kept in order to assess the performance at the operating conditions.

Subsequent to each shut-down the lines and vessels were inspected for evidence of wear, corrosion, errosion, deposits of coke or other solid materials and stress or temperature damage.

The equipment performance assessment was completed by analysis of equipment related problems after each experimental run.

The two types of equipment problems which were encountered in the work performed to date are:

problems related to equipment design, such as condensor plugging, insufficient or excessive heating, reactor coking
poor performance connected to mechanical problems such as plugging, seal leaks, valve failures, erosion.

Recurrent difficulties were experienced in slurry pressure measurement due to plugging of capillaries and valve failures due to erosion and excessive wear of the pressure let-down valves.

Equipment modifications, design changes and notes related to equipment performance of each module will be described below.

6.1 SLURRY PREPARATION AND FEED MODULE

The coal and solvent blending was a lengthy operation in the initial stages of the experimental program, due to insufficient agitation when only a relatively low speed multiblade stirrer was used. The following modifications were made in order to correct this deficiency:

- the existing stirrer was replaced by a fast propeller type stirrer.
- a recirculation loop including a high flow pump (Hayward Gordon model FH432, gear pump), heat tracing and temperature control was added to M2X1 slurry preparation tank.

Repeated failure of the high-pressure-feed pump check valves caused interuptions of the experiments and in one case the complete stoppage of a run. This situation was corrected by a complete redesign of the feed loop: The slurry recirculation lines were redesigned in order to avoid the possibility of coal settling or slurry solidifying. The modifications included relocation of the vessels and high pressure pump in order to smooth the curves and avoid unnecessary lengths of lines. All lines were heat traced using temperature controlled electic heat tape. In-line thermocouples were added close to the high pressure pump inlet.

An additional high pressure pump (Milton Roy, piston, model MR1-84-92SM metering pump) was installed as back-up for the Bran and Lubbe feed pump and the piping was redesigned to allow for the easy switching from one pump to the other.

Extensive maintenance was required to correct or minimize shaft-seal leakage on the slurry pumps.

The main recycle pump (Viking, centrifugal), supplied with graphite-asbestos packing, developed seal leaks which could not be corrected by usual methods. A replacement of the packing with the same type resulted in packing failure after 144 hours of operation. A complete inspection of the pump revealed slight damage to the shaft (scoring). After the necessary repairs the graphite asbestos packing was replaced with teflon rope. The pump has operated in excess of 150 hours since, requiring only normal adjustments.

The gear recirculation pump (Hayward Gordon) was purchased equipped with a mechanical seal. This type of seal failed after 48 hours and was replaced with a standard graphite-asbestos type packing. It has operated approximately 150 hours without failure.

The high pressure piston pump (Bran and Lubbe) used for slurry feed developed recuring leakage at the packing and check valve failures. The packing seal recommended by manufacturer (teflon base) did not give the expected performance and leakage occured after periods of operation varying between 24 and 36 hours and complete packing failure occured after 80 to 120 hours.

The check valves (double ball type with tungsten carbide balls and seats) failures were attributed to two causes - plugging with solid particles and wear. Periods of operation varying between 8 and 40 hours were recorded before failures occurred.

Installation of a back-up pump (Milton Roy MR-1-84-928M) was a very satisfactory solution to feed-pump problems. Although having similar seal packing and check valves type, the new pump offered more reliable performance. The seal packing had to be replaced only after 220 hours of leak free operation. The check valves were changed after each run (approximately 70 hour of operation) as a preventive maintenance procedure although no failure was experienced during runs. After these modifications the slurry feed module operated satisfactory and did not present any more mechanical problems even when tested with slurry having an apparent viscosity in the order of 4000 minPa at 59°C.

6.2 FRESH GAS AND GAS FEED MODULE

In search of better measurement and control of the gas flow through the system, a number of modifications were undertaken during the year. These relate to fresh gas inlet as well as flow control and measurement of gas streams after the reactor.

In the fresh gas inlet lines sequentially activated control valves were installed on the hydrogen and carbon monoxide lines. The operation of the valves is controlled by a system of timers and the relative ratio of the two gases is controlled by the length of time the respective valve stays open. This system proved to work very well in the tests conducted. The micrometric valves and rotameters are still in place but their usage is very much reduced.

Pressure gauges were installed on the two gas storage tanks (M6X1 and M6X2) and on the hydrogen line to the compressor.

The low pressure nitrogen line was separated from the compressor circuit in order to avoid completely the possibility of hydrogen penetrating the inert gas system in case of a check valve malfunction.

Additional differential pressure flowmeters were installed on the lines to the scrubber and scrubbed gas recycle into M6X1. The flow meters have instant reading local displays as well as integrators in the control panels with cumulative readouts of total gas flows.

In order to allow for separate measurement of M3X3 and M4X6 off-gases a separate line and gas meter were installed for the M3X3 light product collector.

Due to the relatively small scale of the PDU and the design of the pressure letdown system (operation of valves on/off as opposed to throtling), the gas flows throughout the system are oscitlating frequently because of slight pressure variations caused by letdown valve opening. At these conditions, gas flow measurement by differential pressure device is probably not the ideal solution but it was adopted and used for lack of a more accurate system. Future work programs will include an extensive effort into the redesign of the gas system with the objective of obtaining better gas flow control.

The diaphragm gas compressor failed (the leak detection system caused compressor to stop) after less than 100 hours of operation due to "O" ring and diaphram failure. This became a recurring problem in future runs. "O" ring failure at the head-diaphram seal occured every 90-120 hours. A second set of SS diaphrams failed after 100 hours and the change from Buna-N to disogrin "O" rings did not provide a solution. Inspection by the manufacturer's representative and our staff revealed two major problems.

(a) diaphram material not up to specifications
(b) a small scratch across the bottom of the ring land.

Both problems were corrected and the compressor has operated for 140 hours to date without a failure.

Gas Scrubber

The sonic level indicators installed on the scrubber according to the manufacturer's instructions performed erratically and only after considerable effort and numerous changes in the mode of installation did it reach the expected performance. In the final configuration the two sensors are fixed on a high-pressure reinforced-nylon line installed externally along the length of the scrubber and connected to the scrubber at both ends. A timer actuated control valve at the bottom of the scrubber controls the flow of caustic solution out of the scrubber. An interlocked system of actuated valves was added in order to allow for taking gas samples without upsetting the scrubber operation.

With these modifications the scrubber performance was satisfactory.

An inspection of the tower's internals after 500 hours did not reveal any corrosion or damage to the packing.

6.3 REACTOR MODULE

The slurry preheater appeared to be operating close to its upper limit in order to maintain the slurry outlet temperature at 280°C when liquid flow was above 9 kg/hr. No coking was observed in the slurry preheater but a severe plug developed a slurry containing over 40% solids wasted. The preheater was then replaced and at the same time some modifications were done to the initial design. These included installation of a more powerful heater (1.2 kw instead of 1.0 kw) and the use of an aluminium core for more uniform and faster heating and easier replacement of the electric cartridge.

A sampling system of interlocked actuated valves with an intermediary small high pressure vessel was installed after the preheater.

The performance of the upflow tubular reactor was by in large satisfactory. In the range of conditions tested the reactor parameters were stable and no solids accumulation or deposits were found after runs, except for two instances when coking occurred.

In the first instance the run had to be aborted due to the plugging of the reactor by coke. Run No. 9 was scheduled to test lignite conversion at 460°C temperature using the Wilsonville hydrogenated solvent and hydrogen. In order to reach the higher temperature, the reactor heaters were replaced with more powerful heating jackets. Three hours into the run the temperature pattern in the zone 2 and 4 of the reactor became irregular with losses of temperature in zone 2 and unusual peaks in zone 4 followed by short lived returns to the set temperature (see Run 9 history in Appendix No. 1). After one more hour the temperature in zone 4 ran away exceeding 580°C at which time the emergency shut down procedure was initiated and the run was stopped.

A post mortem analysis of the run indicated that three factors contributed to the coking in this instance:

- use of a lighter start-up solvent resulted in higher slurry vaporisation and consequently a much lower liquid space velocity
- higher gas flow also increased the vaporized fraction
- use of the more powerful heaters concurrent with a lower liquid space velocity resulted in higher wall temperatures.

The inspection of the reactor's interior after the run revealed presence of two zones of coke.

Corrective measures taken after Run No. 9 included the installation of skin thermocouples for measuring the outside wall temperature along the length of the reactor, low and high level alarms on the reactor and inside temperature controllers.

The subsequent runs were conducted at 440°C and the start-up solvent used was anthracene oil. Reactor coking reoccurred in Run 11. During the shut-down inspection of the reactor, it was found that an annular layer of coke had deposited in Zone 2 and Zone 3 mainly. The lower portion of the coke deposit consisted of porous material and the upper portion was mainly very hard coke. The cause of coke formation in this instance appears to be the higher concentration in the slurry of asphaltenes and preasphaltenes which have a higher propenisity for coking and the higher viscosity of the slurry which interfered with the gas-slurry mixing and with the heat transfer.

A major mechanical problem in the initial runs was the reactor seal leakage at high temperatures and seizing on cooling. An inspection of the closure parts revealed a number of scratches and inadequate machining. The defective parts were remachined by a local machine shop and the problems disappeared.

Repeated plugging of the light ends condensor with waxy or crystalline deposits which resulted in loss of gas flow was resolved by removal of the condensor and modification of the light product receiver M3X2. A water cooled temperature controlled mantle was installed at the exterior of M3X2. As a result, in the last two runs the condensor plugging did not occur.

The low pressure hot receiver M4X5 was modified internally after the run 4 by the addition of baffles and extension of the inlet pipe to avoid entrainment of heavy product as mist into the gas stream directed to M4X6. In the initial runs, heavy oil was repeatedly entrained causing plugging of the line and condensor.

An automatic liquid sampler consisting of a system of interlocked valves was added to the pressure let down system.

6.4 VALVES

Failure of manual valves has been spotty and usually due to improper operation or severe service. Great difficulty has been experienced in opening high pressure slurry valves quickly enough to prevent seat damage.

Where possible automatic valves have replaced manual ones for process control.

The actuated air to close diaphram valves on the blowdown system would not seal after a few operations and were r laced with the air to open type. These sealed satisfactorily but leakage around the diaphram could not be stopped.

The gas inlet valve to the reactor, also a diaphram, air to close AE (Autoclave Engineering) valve was replaced with an AE piston type. The first valve received had a warped housing which caused the piston to jam. Its replacement has operated satisfactorily.

The letdown system performed well but the life of the Badger Meter Research valve stem and seat set (tungsten-carbide) was predictably short (approximately 72 hours). Because of the abrasiveness of the slurry a perfect seal is imperative. In one case an undetected leak eroded the bonnet of the valve.

The valves, located downstream of the 50 ml letdown vessel had a life span of approximately 350 hours. The stelite ball stems of these valves outlasted the SS seats in most cases.

6.5 VACUUM DISTILLATION MODULE

The unit was completely redesigned before being used for the solvent recycle run.

The modifications consisted of:

- Heating mantle was changed to accomodate a bottom valve
- Additional valves for vacuum charging of the feed and direct unloading of the residue without prior cooling, were installed on the boiling pot
- The glass distillation column and condensor were replaced by stainless steel column and condensor.

After the modifications, the time required for the distillation of a 20 kg batch was reduced to 2 1/2 hours down from 4 hours.

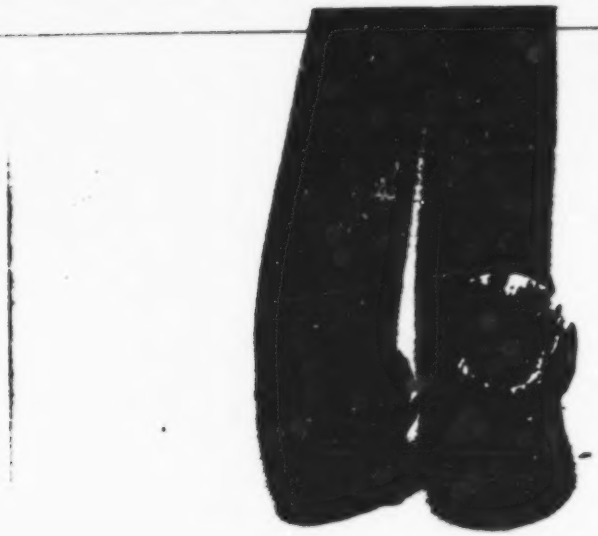


PHOTO NO. 1: Cross-section of the 90° Bend Between the Metering Pumps and Slurry Preheater does not Present Errosion After Hours of Operation

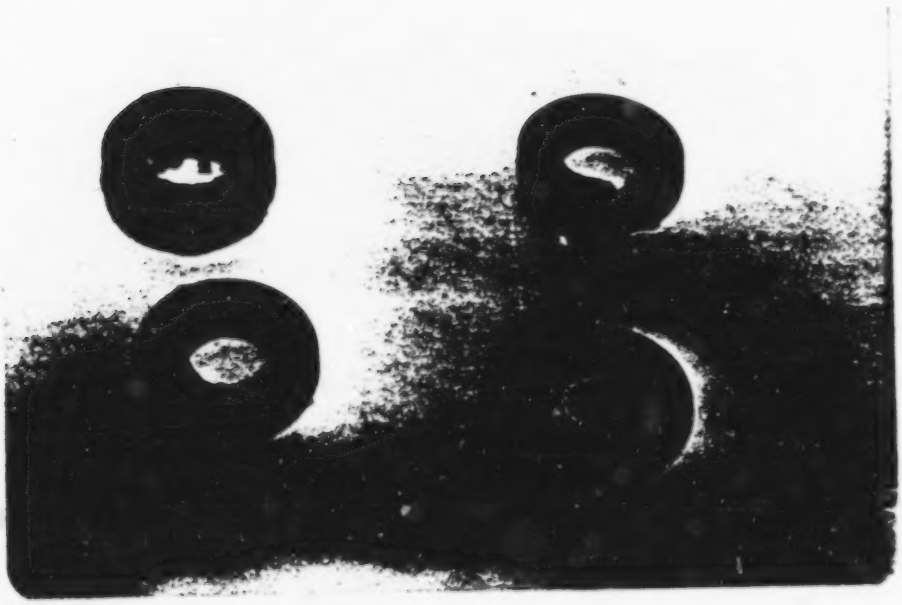


PHOTO NO. 2: Packing Removed from Bran and Lubbe Pump shows wear due to coal slurry

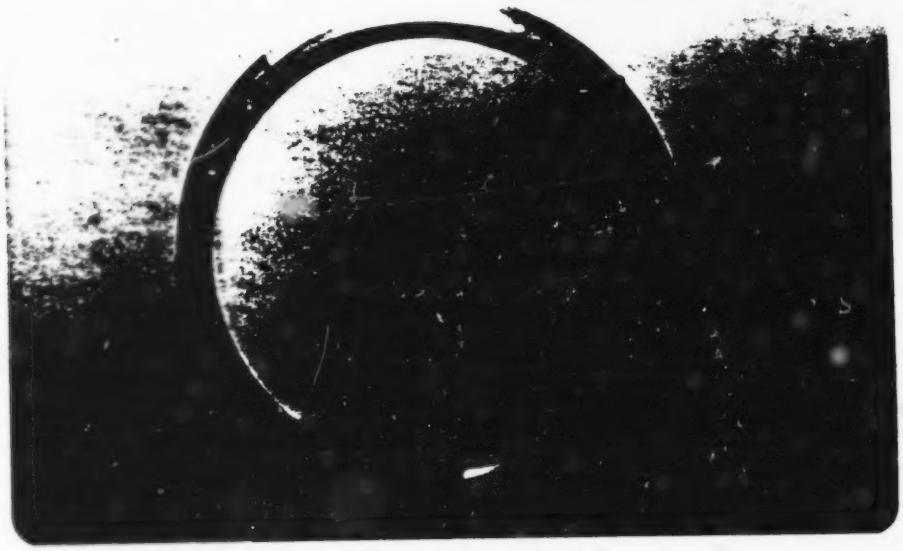


PHOTO NO. 3: Etching Due to Slurry Leaks on Mixing Chamber Sealing Ring

PHOTO NO. 4: Errosion Damage to Reactor Closure Ring

PHOTO NO. 5: Pressure Let-down Valve - Errosion of stem and bonnet occured due to slight leaks around the stem and seat

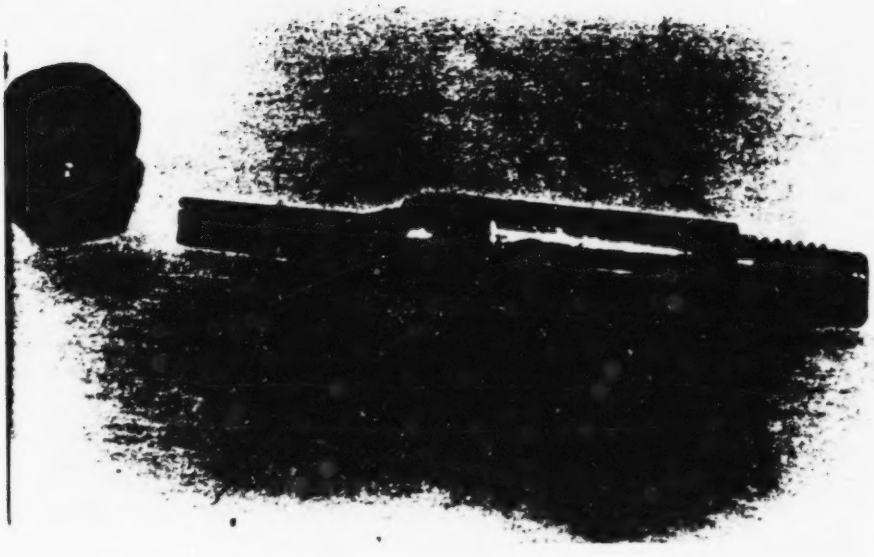


PHOTO NO. 6 Errosion around the stem of a pressure let-down valve

PHOTO NO. 7 Brass tubing on the gas meter line fractured between ferrules

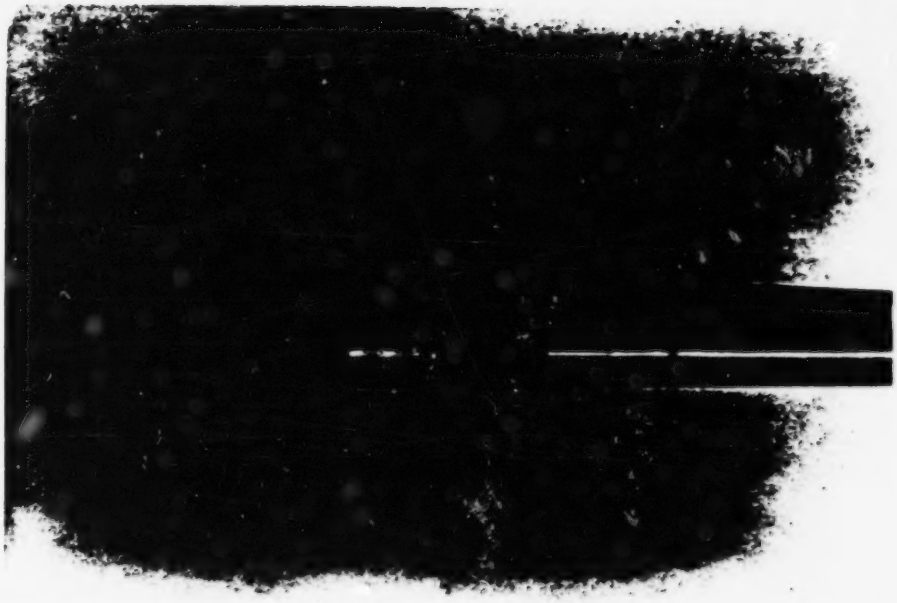


PHOTO NO. 8 Errosion of the Blow-Down Valve Stem

PHOTO NO. 9 Cracks occured in the polycarbonale filter housing before the off-gas gas meter

PHOTO NO. 10: Pressure Let-down Valve - Errosion of the tungsten carbode insert. The brocken stem probably due to misalignment.

7.0 REFERENCES

1) Liquefaction of Low Rank Coals, Report for EMR, Beak Consultants Limited, May 1978.

2) Liquefaction of Low Rank Coals, Report for EMR, Sandwell Beak Research Group, 1980.

3) Production of Oil from Canadian Low Rank Coals, Report for EMR, Sandwell Beak Research Group, 1982.

4) Thermal Hydrocracking of Athabasca Bitumen: Correlation of Reactor Voidage in Vertical Two-Phase Flow. CANMENT Report 77-48; A.M. Shak, B.B. Pruden and J.M. Denis.

5) Thermal Hydrocracking of Athabasca Bitumen: Computer Simulation of Feed and Product Vaporization. CANMENT Report 78-4; D.J. Patmore, B.B. Pruden and A.M. Shah.

6) The Nature and Origin of Asphaltenes in Proposed Coals: EPRI Reports AF-480 1977-1979, D.D. Whitehurst, M. Farcasiu, T.O. Mitchell and J.J. Dickert, Jr.

7) Solvent Refined Coal (SRC) Process. Operation of Solvent-Refined Coal Pilot Plant at Wilsonville, Alabama. 1978-1979.

8) Upgrading Solvent Refined Coal by Hydrogenation: J. Caspers, R. VanDriesseu, Presented at 88th National Meeting of the American Institute of Chemical Engineering, Phi. June 8, 1980.

9) Comparative Studies on the Liquefaction and Solubilization Reactivity of Sublituminous Coals. B. Ignasianc, M.P. du Plessis, M. Gliwlarc, D. Carson, paper presented at 64th CIC Coal Symposium, Halifax, 1981.

10) Continuous and Batch Autoclave Liquefaction of Selected Western Canadian Coals, M.P. du Plessis, R. W. Gregory and B. Ignasiak, preprint of paper presented at 39th CCLE Conference, Edmonton, 1980.

APPENDIX I

RUN HISTORY

RUN No. 3 History

Time (minutes)	
0	Unit pressurized to 3,000 psi, heating started.
347	Reactor temperature = 400°C, started pumping anthracene oil with B & L at 15 mm stroke.
411	Gamma-ray level indicator on hot receiver (M3X1) activated.
505	B & L malfunction, inlet valve was plugged. Inlet check valve was changed.
602	B & L still erratic, pressure gauge after B & L plugged.
655	B & L still erratic, all heaters were lowered by 100°C. B & L head taken apart & cleaned.
720	Slurry flow constant.
865	Coal/solvent batch transferred from feed preparation vessel (M2X1) to feed vessel (M2X2).
1060	Experiment 01 begun.
1215	Experiment 01 ended. Reactor temperature raised to 425°C.
1360	Condensor between hot and cold receivers plugged, cooling water was shut off and a 2,000 psi difference across the plug was used to blow it out.
1405	Fitting on reactor exit started leaking badly. Unit was blown down and fittings were reconed.
2365	Pressure back up to 3,000 psi, reactor at 300°C.

RUN No. 3 History

Time (minutes)	
2380	B & L started (13 mm stroke) on anthracene oil.
2449	Gamma level indicator on hot receiver activated.
2635	Coal slurry transferred to feed vessel, reactor at 425°C.
2785	Experiment 02 started.
2875	Let-down valve malfunctioned - not holding pressure. Switched to left leg.
3065	Experiment 02 ended.
3415	Experiment 03 started.
3710	Experiment 03 ended.
3735	Compressor failure, initiated shut down.
3750	B & L packing failed, no flow. Unit blown down.

RUN HISTORY

Run 04 - Lignite & anthracene oil & H_2
Date: 19-21 May, 1981

Run Time (minutes)	Operation
0	20:31h, 19 May, 1981 Unit pressurized to 3,500 p.s.i. Reactors at 45°C.
143	B & L switched on (13 mm stroke).
147	Reactor temperature at 425°C.
212	Gamma level indicator on hot receiver activated.
375	Switch to coal slurry.
581	06:12h, 20 May, 1981 EXPERIMENT 04 started
1300	EXPERIMENT 04 ended.
1451	Thicker slurry added to feed vessel (42 wt % coal instead of 33 wt % used in experiment 04). Slurry flow erratic, plugging problems. Temperature in recirculation feed line increased to 100°C - recirculation worked O.K. after this.
1813	Slurry flow still erratic; unit blown down.

UNIT	EQUIPMENT PROBLEMS AND MODIFICATIONS
Scrubber	Scrubber operation was tested for the first time. The scrubber recirculation pump could not push against 500 p.s.i.; unit must be operated at lower pressures. Inlet of the pump plugged several times and had to be cleaned out. Water from the scubber was entrained into the gas sampling lines when samples were taken. A valve will be added to isolate the scrubber for gas sampling.
D/P flow measurement	The micrometering flow control valve was installed downstream of the D/P cell and reduced signal spiking due to let down activation to a level acceptable for electronic flow integration.
feed module	Feeding was erratic with a slurry containing 42 wt % coal instead of 33 wt % coal. Better heat tracing and insulation will be added to keep the slurry hot and prevent plugging.

RUN No. 5 History

Time (min)	
	Pressure testing and DP cell calibration lasted 14 hours.
000	Started feeding solvent (A.O.) into the system. Turned the heaters on 200°C (preheater) and 300°C reactor. The Bran and Lubbe pump stopped pumping after a few minutes.
248	The B & L pump was cleaned (check valved found plugged), raised the temperature in M2X2 and heat tracing. The B & L was started at 40 mm stroke, on solvent. The heaters turned on 425°C.
263	Reactor pressure = 3500 psi, Temperature 410°C. Reduced the stroke on B & L pump to 13 mm.
289	Prepared a new batch of A.O. & lignite in M2X1.
320	Gamma-ray detector activated.
380	Transfered slurry from M2X1 to M2X2.
405	Evacuated first time M4X5.
418	B & L problems, temperature in the slurry preheater decreased = the slurry flow stopped.
420-898	B & L problems, lowered temperatures throughout the unit, maintained gas flow.
898	Slurry feed restarted at stroke 20 mm.
926	Gamma-ray activated, B & L stroke reduced to 15.
957	Reactor temperatures 410 - 420 - 405 - 400°C.
985	Reactor temperature reached 425°C in all four zones.
1008	Sight glass on the vapour line off M4X5 leaked and it was replaced by a nipple. Slurry recirculation pump leaking at the packing.

RUN No. 5 History

Time (min)	
1035	Prepared a new batch of slurry in M2X1.
1050	B & L stop & go - increased the stroke to 20 mm and the heat tracing temp to 80°C.
1092	Reduced stroke on B & L to 13 mm.
1100	Calculated the hourly slurry flow, found to be too low Increased stroke to 17 mm.
1153	Set B & L stroke at 16 mm.
1185	Started Experiment No. 5.
1228	Transfered slurry from M2X1 into M2X2, no problems with the metering pump. Maintained 425°C and 3500 psi in the reactor.
1467	Ended Experiment No. 5.
1482	B & L pump is leaking badly at the packing. Blew down the unit.
1482-1978	Rebuild the pump, repressurized, raised temperatures to 315°C with A.O. flow through the system.
1978	B & L pumping A.O., reactor conditions = 3550 psi and 260 - 315°C.
2100	Transfered coal slurry into M2X2.
2101	Started feeding slurry at 30 mm stroke on B & L.
2105	Reduced stroke to 17 after.
2223	Reactor conditions 3500 psi and 425°C.

RUN No. 5 History

Time (min)	
2232	Start of Experiment No 6.
2263	Prepared a new slurry (lignite & CD1) in M2X1.
2401	End of Experiment No. 6.
2422	Transfered slurry to M2X2 from M2X1.
2435	Temperature at the preheater outlet dropped, the preheater was plugged. Blew down the preheater - and the pressure differential broke the plug.
2448	Unit back to conditions B & L stroke = 17 min.
2496	B & L stopped pumping - increased the stroke to 30 mm. for three minutes.
2506	Reactor conditions 3500 psi and 425°C, B & L stroke 25 mm Start of Experiment No. 7.
2754	End of Experiment No. 7.

RUN No. 6 History

Time (min)	
000	Started pumping H_2 in the unit and turned heaters on
194	Started the B & L feeding A.O. The reactor conditions are 3000 psi and 430/425/425/390°C.
271	Gamma-Ray indicator activates the let-down valve.
311	Reactor temperature reached 425 in all four zones.
333	Evacuated M4X5 the first time.
408	Started feeding coal slurry.
410	Rupture disk on the pump discharge blew, it was replaced. The pressure gauge on the B & L discharge is probably plugged. Indications are incorrect.
470	Restarted B & L at 25 mm stroke.
491	Leaks developed in the gas lines, retightened.
500	Check valves on the scrubber pump not operating. Bypassed pump and changed the check valves. Leaks on the M5X1 were stopped. The scrubber pump problems persisted for the length of the run. B & L stroke = 13.
596	Additional heater on the slurry preheater burned out. Solids content in sample of the heavy oil (M4X5) = 5.1%
656	Solids content in M4X5 = 7.8%.
678	Filter on the inlet of the scrubber pump plugged with solids. It was cleaned and reinstalled.
712	Solids content in M4X5 = 8.0%.

RUN No. 6 History

Time (min)	
748	EXPERIMENT No. 8 STARTED P reactor = 3010 psi T reactor = 420/425/425/425 Gas flow = 47.0 SCFH Slurry flow = 4.14 Kg/hr.
792	Solids content in M4X5 = 8%
839	Transfered a new batch of slurry in M2X2.
853	B & L seemed to plug, increased the stroke to 20 for 3 minutes, then reduced back to 13.
912	Solids content in M4X5 = 8.3%.
1037	Solids content in M4X5 = 7.8%.
1080	The level indicator in the scubber out of order. Stopped the pump and bypassed the scrubber whipe washing the visors.
1113	Solids content in M4X5 = 7.8%.
	EXPERIMENT No. 8 COMPLETE
1120	Scrubber back in order. Increased stroke in B & L to 25mm.
1135	Packing on the B & L pump started leaking, it was tightened on the run.
1244	Transfered new batch of slurry made with CD_1 as solvent.
1251	Solids content in M4X5 = 12.2%.

RUN No. 6 History

Time (min)	
1252	The B & L pump stopped pumping. The plunger was not moving. It was found that the packing was too tight which made the plastic sleeve coupling that holds the shaft to slip without moving the plunger. Loosened the packing and tightened the nut. The pump was O.K. after that.
1291	Solids content in M4X5 = 11.5%.
1343	Solids content in M4X5 = 12.3%.
	EXPERIMENT No. 9 STARTED. P reactor = 3050 psi T reactor = 420/425/425/426 Gas flow = 53.5 SCFH Slurry flow = 10.3 Kg/hr.
1345	Bypassed the scrubber for five minutes to change filter on the pump inlet.
1392	Solids content in M4X5 = 13.0%.
1427	Solids content in M4X5 = 11.8%.
1477	Bypassed the scrubber for 10 minutes to clean the filter on the pump inlet.
1484	Transfered new batch of slurry into M2X2.
1508	Solids content in M4X5 = 12.3%.
1648	Solids content in M4X5 = 13%.
1663	EXPERIMENT No. 9 COMPLETE
1687	Transfer new slurry into M2X2. Added extra insulation around the reactor, in view of raising the temperature to 440°C.

RUN No. 6 History

Time (min)	
1698	Reactor temperature 440°C in all four zones.
1706	Laces holding the reactor heater burnt off, were replaced by metal bands.
1864	Motor on M2X1 recirculation pump burnt off, it was replaced.
1851	Solids content in M4X5 = 12.2%.
1900	Transfered slurry into M2X2.
1920	Solids content in M4X5 = 11.73%.
	EXPERIMENT No. 10 STARTED. P reactor = 3020 psi T reactor = 420/437/437/437 °C Slurry flow = 10.0 Kg/hr. Gas flow = 56 SCFH
1982	Solids content in M4X5 = 11.59%.
2043	Solids content in M4X5 = 12.52%.
2088	Transfered slurry into M2X2.
2107	Solids content in M4X5 = 10.93%.
2270	EXPERIMENT No. 10 COMPLETED
2303	Transfered slurry into M2X2, lowered back pressure regulator to 2500. Did the same to pressure regulator M6X2.
2381	Solids content in M4X5 = 13.4%.
2415	Solids content in M4X5 = 11.82%.
2499	Solids content in M4X5 = 11.22%.
2511	Transfered slurry in M2X1.

RUN No. 6 History

Time (min)	
2523	EXPERIMENT No. 11 STARTED. P reactor = 2500 psi T reactor = 428/435/438/438°C Slurry flow = 10.0 Kg/hr. Gas flow = 51.5 SCFH
2559	Solids content in M4X5 = 10.77%.
2660	Solids content in M4X5 = 9.95%.
2704	Transfered new slurry into M2X2.
2764	Solids content in M4X5 = 9.75%.
2830	Solids content in M4X5 = 9.5%.
2916	EXPERIMENT No. 11 COMPLETED.
2920	Started normal procedure for unit shut down.

RUN No. 8 History

Time (min)	
	The pressure testing and leak proofing were completed in 6 hours. The DP cell calibration and first step heat up were completed in 6 hours
0	Started pumping Wilsonville solvent using the Milton Roy (M.R) pump. The temperature in the slurry preheater was at 130°C in the reactor zones at 340/310/300/260°C, the pressure was 3500 psi throughout the system, The H2 flow 1500 L/h
85	The gamma ray detector activated the first time
139	The Badger Meter valve on the right leg failed, switched to left leg. The system reached reaction conditions Temperatures °C - slurry out of preheater 285°C - reactor zones 425/426/475/425 °C
235	Started feeding coal slurry: Wilsonville/Lignite 2/1
318	Solids content in M4X5 is 4.21%
328	Prepared a new slurry (same composition) in M2X1
395	Solids content in M4X5 is 6.60%
450	Recirculation pump is leaking at the packing
462	Solids content in M4X5 is 8.56%, gas flow 1200 L/h
499	Solids content in M4X5 is 8.53%
510	STARTED EXPERIMENT No. 15 P = 3500 psi T reactor = 425°C Slurry Flow = 5.8 kg/h Gas Flow = 1036 L/h

RUN No. 8 History

Time (min)	
563	Transfered second batch of slurry into feeding tank M2X2
587	Sampled feed 30.2% solids
612	Solids content in M4X5 is 8.7%
739	Solids content in M4X5 is 8.57%
869	Solids content in M4X5 is 7.9% Prepared a batch of slurry in M2X1 recycle filtrate/coal 2/1
925	ENDED EXPERIMENT No. 15
	Started feeding recycle solvent containing 1.2% solids 22.3/11.0 kg/coal slurry - SECOND PASS Solids content in the feed 35.3%
970	Solids content in M4X5 is 9.2%
1100	Leak detection system shut the compressor off - Released and restarted the compressor
1146	Solids content in M4X5 12.02%
1200	Prepared a new slurry in M2X1 - solvent solids content 2.31% solvent 22 kg/coal 11.0 kg
1219	Solids content in M4X5 11.75%
1261	Transfered slurry in M2X2 - THIRD PASS Solids content of the slurry 32.04
1295	Solids content in M4X5 13.09%
1347	Failure of the M2X2 recirculation pump - motor burned off. Continued feeding with Milton Roy pump
1350	Solids content in M4X5 11.41%

RUN No. 8 History

Time (min)	
1373	Shut off the Milton Roy pump - because of plugging and problems with both recirculation and Milton Roy pump Increased the gas flow through the slurry preheater
1506	Recirculation pump repaired & started
1510	Milton Roy pump restarted
1520	Rupture disk blown-off. The pressure in the system went to 1000 psi. The gas flow was maintained, the rupture disk was isolated and replaced
1535	The rupture disk in place, the unit will be repressurized
1660	The three pumps were in working order, the pressure in the whole system was back to 3500 psi. At this point the pressure relief valve on the scrubber opened and the scrubber pressure went down. It was fixed and:
1682	Restarted feeding coal slurry with the B & L pump
1715	The B & L pump erratic, switched on the Milton Roy pump on 35% stroke
1719	Transfered recycle - coal slurry (22.12 lbs/11.1 coal)
1750-1833	Problems developed with the valve at the bottom of M4X5. The heavy product could not be evacuated for this period - the recycle was not possible. Decided to stop the experiment and start it all over.
1883	Started feeding a slurry prepared with Wilsonville solvent 30 lbs solvent/15 lbs lignite
1862	Solids content in let down product was 11.05%
1930	The M4X5 valve was operational again

RUN No. 8 History

Time (min)	
1967	M4X5 solids 10.03
2060	Transfered a new slurry prepared with Wilsonville solvent and lignite
2090	Solids in M4X5 were 10.07%
2200	Compressor failure due to leaks through the "O" rings lowered the gas flow. Maintained the compressor working on maximum suction (1000 psi), releasing the pressure in the leak detection system periodically until built 5000 psi in the gas storage tank M6X2. At this point by-passed the compressor, the head was disassembled and the "O" rings were changed. The gas flow through the unit was maintained out of M6X2
2213	Prepared a slurry with 29 lbs filtrate and 14.5 lbs lignite in M2X1
2235	The compressor back in operation, the gas flow back to normal
2298	STARTED SECOND PASS With the transfer of the slurry from M2X1
2318	Short period of eratic flow during which the stroke was increased to 50%
2328	Stroke back to 35% on the Milton Roy pump
2442	Prepared a new slurry in M2X1 - 20 lbs filtrate, 10 lbs M4X5 product and 15 lbs coal
2464	Transfered the slurry into M2X2 STARTED THIRD PASS
2467	Transfer complete but some coal remained stuck on the walls in M2X1. In order to remove it 10.8 lbs of M4X5 product was added in M2X1. Stirred for 10 minutes and transfered to M2X2. The final solids concentration in the feed was 28.2%
1350	Solids content in M4X5 11.41%

RUN No. 8 History

Time (min)	
2560	Solids content in M4X5 was 11.33%
2612	Solids content in M4X5 was 10.5%
2672	Solids content in M4X5 was 10.8%
2690-2700	Prepared slurry in M2X1 for the fourth pas using 18.0 lbs filtrate, 13 lbs M4X5 product (as collected) and 15 lbs of coal. The solids content in the solvent was 5.94%. Solids content in feed 31.6%
2719	Transfered slurry in M2X2 STARTED FOURTH PASS
2725	Solids content in M4X5 was 10.6%
2809	Solids content in M4X5 was 10.5%
2838	Air compressor failure - the back-up nitrogen system was activated until the air compressor was back in operation
2860	Solids content in M4X5 was 13.61%
2870	Prepared slurry in M2X1 for the fifth pass using 131bs of filtrate, 14 lbs of M4X5 and 11 lbs of coal. The solids content obtained in the slurry feed was 34.65%
2895	Transfered slurry in M2X2 STARTED FIFTH PASS
2939	Solids content in M4X5 was 14.04%
3045	Prepared slurry in M2X1 for the sixth pass using 6 lbs of filtrate, 20 lbs of M4X5 and 7 lbs of coal. Solids content in the slurry 31.2%
3068	Transfered slurry in M2X2 STARTED THE SIXTH PASS
3115	Solids content in M4X5 was 14.87%

RUN No. 8 History

Time (min)	
3180	Prespared new slurry in M2X1 for the seventh pass using 31 lbs recycle M4X5 and 6 lbs coal. The solids content of the slurry prepared was 27.83
3194	Transfered slurry in M2X2 - STARTED THE SEVENTH PASS
3229	Solids content in M4X5 was 13.8%
3313	Prepared a new batch of slurry for the eighth pass using 12 lbs coal and 27.5 lbs M4X5 not filtered solids content of the slurry was 34.5%
3349	Transfered the slurry in M2X2 STARTED THE EIGHTH PASS
3379	Solids content in M4X5 was 14.72
3480	Solids content in M4X5 was 15.7%. Prepared a new slurry in M2X1 for the ninth pass using 26 lbs M4X5 product not filtered and 9 lbs of coal. The solids content of this slurry was 35.32%
3503	Transfered the slurry in M2X2 STARTED THE NINETH PASS
3580	The solids content in M4X5 was 18.18%
3616	The solids content in M4X5 was 20.9%
3635	Prepared a new slurry product in M2X1 using 34 lbs of M4X5 product unfiltered and 8 lbs of coal. The solids content in this slurry was 34.65%
3676	Transfered the slurry in M2X2 STARTED THE TENTH PASS
3685	Solids content in M4X5 was 22.83%
3862	COMPLETED THE EXPERIMENT and started the normal shut down procedure.

RUN No. 9 History

Time (minutes)	
	The pressure testing and leak proofing were completed in eight hours. The DP cell calibration and first heat up were completed in four hours.
0	Started pumping Wilsonville solvent using the M.R. pump (35% stroke length). The temperature of the reactors four zones were at 250/175/210/190°C. The pressure was 3500 psi throughout the system. The Hydrogen flow was 33SCFH.
58	Gamma-ray counter activated
167	Started scrubber. Caustic soda added to water in M5X1. Scrubber pressure 420 psi.
181	Connected M3X3 to high pressure system.
184	Reactor temperatures 430/460/460/460°C.
191	Transferred slurry from M2X1 to M2X2. Concentration of slurry-coal and Wilsonville solvent.
220	Started experiment 17
302	Recirculation pump of M2X2 leaking. Packing retightened.
433	Let-down system switched to right leg.
420	Temperature of reactor in zone 2 dropped down to 440°C.
465	Emptied M3X3
465	Temperature of reactor in zone 2 back to 460°C.

RUN No. 9 History

Time (minutes)	
470	Temperature of reactor in zone 4 increased to 490°C. Temperature of reactor in zone 2 dropped to 440°C.
475	Temperature of reactor in all 4 zones back to 460°C.
480	Recirculation pump head of M2X2 was smoking. The packing was loosened and an air fan was installed to cool it.
510	Temperatures in the reactor started to run away from the set-temperature of 460°C. All of them increased to 470°C for a couple of minutes. Temperatures in zones 3 and 4 returned to 460°C. Temperatures in zones 1 and 2 continued decreasing.
520	Temperature in zone 1 at 420°C. Temperature in zone 2 at 445°C. Started first distillation.
525	Temperautes in all zones around 460°C.
530	No gas flow was observed. The pressure in the unit increased to 4000 psi. The pressure at the back pressure regulator was at 3580 psi. Probably a plug in the condenser. Reactor zone 4 temperature increased to 520°C. Reactor zones 1 and 2 temperatures started decreasing. Condenser input temperature of gas inlet increased to 400°C. The plug was removed by creating a pressure difference by employing M3X3.
533	Temperature in zone 4 was 480°C. Temperature in zone 3 was 470°C. Temperature in zone 2 was 370°C. Temperature in zone 1 was 360°C.
553	Temperature of zone 4 went up to 550°C. Temperatures of other zones around 430°C. Liquid and gas flows were normal. Temperature settings of all zones were lowered.

RUN No. 9 History

Time (minutes)	
580	Emptied M3X3. Back pressure regulator at 2800 psi. Refilled M3X3 with gas. Zone 4 temperature was at 480°C.
590	Pressure in the reactor went up to 4600 psi. The M.R. pump was shut. The pressure in the reactor returned to normal, 3600 psi.
597	The M.R. pump was switched on. Pressure in the reactor increased to 4100 psi in one minute. Temperature of all zones around 460°C.
609	Pressure in the reactor increased to 4500 psi. Temperatures of zones 3 and 4 around 460°C. Temperature of zones 1 and 2 around 420°C. The M.R. pump was switched off. M2x2 was emptied and 30 lbs of Wilsonville solvent were added.
637	Started pumping Wilsonville solvent. Pressure in the reactor 4100 psi. The M.R. pump did not require priming. M2X2 recirculation pump was smoking. Temperature in all reactor zones around 460°C.
655	Pressure in reactor at 4500 psi. M.R. pump was swithced off. The gas flow was stopped.
718	End of first distillation.
730	Pressure in reactor reduced to 1500 psi. Reactor blow-down.
837	Started second distillation.
987	End of second distillation.

RUN No. 10 History

Time (minutes)	
0	P = 3500 psi H_2 Reactor T = 70-100°C Started pumping anthracene oil with Milton Roy pump set at 35% of full stroke.
33	Scrubber started.
74	Problems maintaining constant solvent flow.
111	Switched to B & L pump.
152	Gamma-ray detector activates right leg of let-down.
197	B & L pump motor started rattling; switched back to Milton Roy pump.
362	Transfered coal slurry to feed vessel (M2X2) Rezeroed timer.
	First pass started
0	Reactor T = 400-436°C Slurry flow = 7.2 kg/h; pump stroke was readjusted.
120	Reactor temperatures: Zone 1 = 425°C Zone 2 = 435°C Zone 3-4 = 440°C Milton Roy stroke = 32%
167	THF insolubles in M3X1 = 9.0%
248	THF insolubles in M3X1 = 9.0%
260	Distillation started on 20.25 kg of M4X5 product.
322	THF insolubles in M3X1 = 8.7% H_2O content in M3X1 = 2.3%.

RUN No. 10 History

Time (minutes)	
448	First distillation completed. Total distillables were 78%. Solvent fraction (250-420°C) was 76%.
471	THF insolubles in M3X1 = 8.9%.
505	Gas regulator to M4X5 flow meter plugged. It was replaced.
555	Second distillation of heavy product (16.5 kg) was started.
653	Distillation completed - solvent fraction was 61%.
780	Second pass was started. The slurry solvent was made up of 50% distillate and 50% heavy product directly from M4X5.
800	THF insolubles in M3X1 = 9.0%.
840	Third distillation was started (22.0 kg).
914	THF insolubles in M3X1 = 10.2%.
980	THF insolubles in M3X1 = 10.5%.
982	Scrubber pump failed due to plugging of water filter. The filter was cleaned and replaced.
1069	THF insolubles in M3X1 = 10.7%.
1070	Erratic slurry flow for about 10 minutes. M4X5 and M5X1 gas meters were turning backwards. Lines to the meters were leak tested but no leaks were found.
1073	Third distillation was completed - solvent fraction was 68%.
1214	Fourth distillation was started (17.9 kg). The solvent fraction yield was 66%.
1221	Third pass was started.
1260	THF insolubles in M3X1 = 12.2%.

RUN No. 10 History

Time (minutes)	
1340	Short circuit in gas preheater element. Repairs were done immediately with no temperature losses in the reactor.
1440	THF insolubles in M3X1 = 12.6%.
1551	Fifth distillation was started charge was 18.8 kg solvent fraction yield was 64%.
1600	Fourth pass was started.
1620	Leaks were found in the scrubber system.
1688	THF insolubles in M3X1 = 11.0%.
1730	Sixth distillation was started charge was 17.6 kg solvent fraction yield was 62%.
1770	THF insolubles in M3X1 = 10.8%
1930	Seventh distillation was started charge was 19.5 kg solvent fraction yield was 65.6%.
1984	Fifth pass was started
2210	THF insolubles in M3X1 = 11.7%.
2278	Let down system switched to manual to look for leaks in M4X5-M4X6 area. Large leak found at M4X6 closure. Started working on closure.
2370	M4X6 was resealed
2397	Sixth pass was started
2435	THF insolubles in M3X1 = 12.1%
2500	THF insolubles in M3X1 = 11.3%

RUN No. 10 History

Time (minutes)	
2520	Eighth distillation started charge was 18.3 kg. solvent fraction yield was 59%.
2561	THF insolubles in M3X1 = 10.1%.
2645	THF insolubles in M3X1 = 11.1%.
2764	Seventh pass was started.
2780	THF insolubles in M3X1 = 12.8%.
2858	Ninth distillation started charge was 19.9 kg solvent fraction yield was 64%.
3046	Milton Roy pump developed a bad leak. The packing was tightened and pumping returned to normal.
3156	THF insolubles in M3X1 = 11.6%.
3158	Eighth pass was started
3245	Leak in pressure control unit of gas compressor. The control unit was by passed for the remainder of the run.
3250	Tenth distillation was started charge was 19.2 kg solvent fraction yield was 59%.
3383	THF insolubles in M3X1 = 11.8%.
3415	Erratic flow for a few minutes
3537	Ninth pass was started.
3620	THF insolubles in M3X1 = 10.9%.
3907	Tenth pass was started.
3981	THF insolubles in M3X1 = 12.4%.
4297	Started normal shut-down procedures.

RUN No. 11 History

Time (minutes)	
0	Pressure = 3550 psi.
26	Milton Roy pump started - anthracene oil.
92	Gamma-ray detector activated right leg of let down.
140	Reactor temperature was 440-480°C.
199	Transfered coal slurry to feed vessel M2X2. Rezeroed time.
0	First pass was started. Reactor temperatures wer 410/440/440/440°C.
110	Reset Milton Roy stroke to 35% for 6 kg/h slurry flow.
221	THF insolubles in M3X1 = 7.6%.
242	Right leg of let down failed - switched to left leg.
269	First centrifugation of heavy product - 11.0 kg.
403	Second pass was started with slurry made of recycle solvent.
467	Experienced gas flow problems. Line between M3X1 and M3X2 was plugged. Stopped slurry and gas flow and blew out the plug with a high pressure difference across it.
600	Slurry and gas flows restarted.
775	Line plugged again. Blew out the plug in a few minutes.
794	Second centrifugation of heavy product - 20.1 kg.
850	Heating of M3X1 vessel was increased to prevent plugging.
916	Third pass was started.
989	THF insolubles in M3X1 = 12.1%.
1026	Scrubber was shut off to change the filters.

RUN No. 11 History

Time (minutes)	
1034	Scrubber was put back in operation.
1077	Third centrifugation was begun.
1125	M3X3 regulator was removed and cleaned.
1152	M3X3 regulator was replaced.
1283	THF insolubles in M3X1 = 13.5%.
1322	Fourth pass was started.
1500	Fourth centrifugation was begun.
1621	THF insolubles in M3X1 = 14.6%.
1664	Fifth pass was started.
1842	THF insolubles in M3X1 = 18.3%.
1860	Fifth centrifugation was begun.
2041	Sixth pass was started.
2106	THF insolubles in M3X1 = 19.2%.
2196	Sixth centrifugation was begun.
2200	THF insolubles in M3X1 = 18.3%.
2673	Seventh pass was started using M4X5 product without coal.
2750	THF insolubles in M3X1 = 18.5%.
2805	THF insolubles in M3X1 = 17.4%.
2936	Eight pass was started using M4X5 product and red mud as catalyst but no coal.
3095	THF insolubles in M3X1 = 18.4%.
3137	THF insolubles in M3X4 = 19.3%.
3146	Started normal shut-down procedures.

APPENDIX II

DEVELOPMENT OF A PDU SYSTEM FOR THE SEPARATION OF SOLIDS FROM COAL-DERIVED LIQUEFACTION PRODUCT

APPENDIX

DEVELOPMENT OF A PDU SYSTEM FOR THE SEPARATION OF SOLIDS FROM COAL DERIVED LIQUEFACTION PRODUCT

The solids separation aspect of the program was given a large share of the effort. Small scale continuous PDU's for the direct liquefaction of coal can give good indications of larger scale operations when operated on a continuous solvent recycle mode. Such systems are generally complex and difficult to operate due to the problem of solids separation, solvent quality and solvent demand for coal slurrying.

Only when operated at full solvent recycle at steady-state are product yields and distributions realistic of larger scale operations.

The economics of direct liquefaction is very dependent on the quality and marketablility of the coal-derived liquids. Until such time as steady-state coal liquids can be produced in sufficient quantities to assess their quality and characteristics, the value and marketability of coal derived products remain speculative.

A number of investigations of liquefaction of Canadian coal presently underway would like to conduct testing of various coals in a continuous liquefaction pilot plant. The value of these testing programs would be enhanced if a reliable recycle system would be available in Canada.

Even on a PDU scale (i.e. with little regard to efficiency) solids separation is a difficult task due to:

(a) the wide particle size range with a large fraction below 1 μm,

(b) the relatively high viscosity of the liquid phase even at elevated temperatures,

(c) the small difference between the density of the liquid phase and the solids,

(d) the 'nature' of the liquid and solids which probably leads to a complex interaction between the particles and surrounding liquid.

The objective of developing a process for solid-liquid separation in conjuction with lignite liquefaction was approached in two steps.

(a) develop a system capable of producing a traction for recycle and operate the PDU with recycle for long enough time to reach steady state,

(b) using the steady state product develop design basis for a system capable to handle the solids separation for a continuous operation of a coal liquefaction and address the problems of solvent quality and solvent balance.

A solid-liquid separation system is at the heart of any coal liquefaction process in combination with the liquefaction process in combination with the liquefaction or hydrogenation reactor. The operation and performance of these two unit operations are mutually dependent. Also the type of obtained product slate is mainly a function of what happens in these two operations.

OBJECTIVES

The above outlined needs lead to the following objectives for the first year of the PDU operation:

(1) to develop a solids separation system(s) that made possible the continuous operation of the PDU unit in a recycle mode,

(2) to evaluate the effects of different PDU solids separation systems on the operability of the PDU plant and type of resultant products,

(3) to initiate the development of a solids separations system for full scale use based on PDU experience.

PDU SOLIDS SEPARATION

Separation of the solids has been and still is the subject of much research and development. As a first step in the search for a suitable technique for the SBRG PDU unit a literature review was carried out. The findings are presented below.

Literature Review

Reviews of the development work of solid-liquid separation technology in coal liquefaction processes have been presented by other workers, as for example by Shou J.K.P. and Collins D.J. (in Proceedings of the Coal and Coke Sessions of the 28th Can. Chem. Eng. Conf. in Halifax, Nova Scotia, Oct. 22-25, 1978; Publ. by Can. Soc. for Chem. Eng., 906-151 Slater, Ottawa, Ont., K1P5H3). An extensive review is therefore not repeated here. However, for completeness, the essence of the areas of investigation are presented and discussed below.

Broadly, the areas of investigation involve the use of the following unit operations or a combination of these:

(a) Mechanical
  (1) filtration
  (2) centrifuge
  (3) hydroclone
  (4) magnetic

(b) Evaporation
  (5) distillation
  (6) coking (carbonization, pyrolysis)

(c) Solvent-aided Separation
  (7) antisolvent deashing
  (8) solvent extraction/leaching
  (9) critical solvent deashing

Filtration provides for a high liquid yield by means of washing with a light oil and subsequent recovery of the light oil by drying of the filter cake and separation from the filtrate. A dried filter cake contains typically 5-10% liquid product. That is, the cake consists of 90-95% solids and 5-10% of the desired liquid product on a dried solids cake basis. Filtration, although it has a very good liquid yield, still has as drawbacks: slow filtration rates, cost of pre-coat materials, and handling of the filter cake. Centrifuges do not achieve as sharp a separation of the solids as by filtration. Also mechanical problems arise in the continuous removal of solids due to their abrasive and adhesive (sticky) properties. A centrifuged 'solids cake' typically still contains 50-55% of liquid product on a total cake weight basis. Hydroclones achieve an even less sharp separation and are at best used for pre-thickening purposes in combination with other unit operations. Magnetic separation processes can only remove part of the solids. The organic compounds of coal are diamagnetic while the ash (inorganic mineral matter) compounds are paramagnetic which makes it possible to separate these by magnetic means. However, the unconverted coal cannot be separated.

Distillation or evaporation is a possible means of separation. Very sharp separation can be achieved given that liquid carry-over is minimized. The bottoms of such units typically contain 55% of liquid product (i.e. 45% solids). Coking is another process which provides a sharp separation. However, a considerable amount of liquid product is lost due to gasification of the light oil fraction and coking of the heavier liquid hydrocarbon products.

Anti-solvent deashing is the process whereby the solids are co-precipitated with the asphaltene/pre-asphaltene portion of the liquid liquefaction product due to the solution equilibrium imbalance brought about by the additions of an anti-solvent. The precipitated solids phase typically contains 55-60% liquid product. Solvent extraction and leaching have been used for removal of only part of the solids. Coarser and heavier particles need to be removed by other means. Critical solvent processes affect separation by the greatly enhanced dissolving power of solvent in the range of pressure and temperature near the critical values for the solvent. By proper choice of solvent, pressure, and temperature such a process can effectively separate solids, asphaltenes/pre-asphaltenes, and oils from each other. After recovery of the critical solvent by evaporation the solids phase typically still contains 35-40% liquid product.

Lab Scale Experimental Investigation

To supplement the 'know-how' obtained from the literature review, several lab scale experiments were carried out. The provide a means of familiarization with the to be separated material under different conditions, and a verification of applicability of literature findings to lignite-derived product. The experimental procedures and results of these tests are presented below in table form.

TABLE 1: SETTLING TESTS

EXPERIMENT NUMBER	SCHEMATIC OR DESCRIPTION OF APPARATUS	SUMMARY OF EXPERIMENT PROCEDURE	SUMMARY OF EXPERIMENTAL RESULTS
13/11/81-1		-vessel was partially filled a depth of u 7" with M4X5 product from run 05 exp. 06 -vessel contents were kept at 150-180°C and 150-200 psig for one hour -after the one hour settling time the vessel was emptied the contents collected in a top, middle, and bottom fraction	fraction: top, middle, bottom volume %: 83, 17 THF insolubles (weight %): 9.4, 9.8, 11.4
13/08/81-1	-laboratory test tube	-test tube was filled with M4X5 product from run 05 exp. 06, heated in an oil bath from room temperature to 180-210°C and kept at this temperature for 3 hours	fraction: starting material, top, bottom weight %: 100, 82.5, 17.5 THF insolubles (weight %): 9.69, 8.85, 15.57

SBRG

TABLE 1: (cont'd) SETTLING TESTS

EXPERIMENT NUMBER	SCHEMATIC OR DESCRIPTION OF APPARATUS	SUMMARY OF EXPERIMENTAL PROCEDURE	SUMMARY OF EXPERIMENTAL RESULTS
13/08/81-2	-laboratory test tube	-same as for 13/08/81-1 except that the starting material was made up of 1/3 W/W proportions of anthracene oil (AO) and M4X5 product from run 05 exp. 06	

fraction	volume %	THF insolubles (weight %)
starting material	100	7.47
top	80.7	2.19
bottom	19.3	14.35

EXPERIMENT NUMBER	SCHEMATIC OR DESCRIPTION OF APPARATUS	SUMMARY OF EXPERIMENTAL PROCEDURE	SUMMARY OF EXPERIMENTAL RESULTS
13/08/81-3	-laboratory test tube	-same as for 13/08/81-2 except that the ratio of AO/M4X5 was 4/1 W/W	

fraction	weight %	THF insolubles (weight %)
starting material	100	2.01
top	84.1	0.98
bottom	15.9	7.96

TABLE 2: CENTRIFUGE TESTS

Typical Experimental Procedure:		-starting material was put into a centrifuge tube(s) which was then heated to temperatures, placed in a laboratory centrifuge (1200-1900 G), and rotated at 3000 RPM for a certain time -after stopping the centrifuge the flowable top fraction was decanted from the centrifuge tube and both top and bottom fractions were then analyzed					
Experiment Number		4/12/81-1	3/12/81-1	21/12/81-1	30/11/81-1	22/11/81-1	6/1/82-2
Experimental Conditions		150	150	220	250	250	250
temperature (°C)		120	120	120	125	125	125
time at max. speed (min)		5	30	5	30	5	5
speed (RPM)		3000	3000	3000	3000	3000	3000
Feed Material		M4X5 run 05 exp.07	M4X5 run 05 exp.07	M4X5 run 05 exp.07	M4X5 final pass run 08	M4X5 final pass run 08	top fraction of 22/11/81-1
composition WT%	O*	77.3				52.0	62.9
	A	7.7	7.7	7.7		13.4	13.9
	PA	5.7	5.7	5.7		9.7	10.1
	S	9.3	9.3	9.3	24.5	25.0	13.1
Centrifuged Material					50.1		
Top	Weight %	62.8	74.7	73.3	7.2 42.9	71.4	69.3
composition WT%	O	87.0	85.5	84.1		61.5	67.0
	A	6.2	7.3	8.6		12.5	14.0
	PA	6.0	7.1	6.5		10.9	10.1
	S	0.88	.09	0.85	0.66 5.21	15.1	8.9
Bottom	Weight %	37.2	25.3	26.7	49.9	28.6	30.7
composition WT%	O	65.8	58.7	56.8		34.2	51.2
	A	5.8	3.0	4.5		6.7	13.2
	PA	2.8	3.1	4.2		5.9	6.9
	S	25.7	35.2	34.5	25.0 41.9	53.2	28.7

* O - hexane soluble material
A - toluene soluble - hexane soluble material
PA - THF soluble - toluene soluble material
S - THF insoluble material

SBRG

TABLE 3: VACUUM EVAPORATION TESTS

Experiment Number	Summary of Experimental Procedure	Summary of Experimental Results
- /9/81-1	-M4X5 product from exp. 09 run 06 was evaporated under vacuum (up to 2 mmHg) to an actual temperature of 300°C in the PDU evaporator	-the bottoms fraction is flowable at 240°C

fraction	weight %	O (W%)	A & PA	S (W%)
distillate	54.8	100	-	-
bottoms	44.2	38.4	26.7	35.0

Experiment Number	Summary of Experimental Procedure	Summary of Experimental Results
- /9/81-2	-same as above	-the bottoms fraction does not flow at 290°C

fraction	weight %	O (W%)	A & PA	S (W%)
distillate	69.1	100	-	-
bottoms	30.0	7.8	37.3	54.8

Experiment Number	Summary of Experimental Procedure
18/12/82-1	-a 'centrifuge cake' obtained from M4X5, exp. 07 run 08 material was evaporated under vacuum (up to 0.2 mm HG) in a flask which was heated in an oil bath up to 242°C

fraction	weight %	O (W%)	A (W%)	PA (W%)	S (W%)
centrifuge cake	100	55.9	6.5	3.0	34.6
distillate	42.5	99.6	0.4		
bottoms	57.6	9.4	5.1	7.5	78.0

SBRG

SBRG

TABLE 4: LIQUID CYCLONE TESTS

Experiment Number	Summary of Experimental Procedure and Conditions	Summary of Experimental Results
8/1/82-1	-M4X5 product from run 08 final pass plus a solvent (1/1 W/W) were fed from a heated vessel under nitrogen pressure though a liquid cyclone (Doxie type A by DorrOliver), and the overflow and underflow were collected in separated vessels for analysis -the experimental conditions for exp. 8/1/82-1 were: (a) feed rate 5.0 kg/min (b) pressure drop 1.55 MPa(225 psi) (c) temperature of feed material 260°C	fraction / weight % / S (THF insolubles) overflow / 38.5 / 13.2 underflow / 61.5 / 18.5 feed / 100 / 16.5
8/1/82-2	-same as for experiment 8/1/82-1 except that: (a) feedrate 3.6 kg/min and the solids concentration of of the feed was approximately 15.1% instead of 16.5% as for experiment number 8/1/82-1	fraction / weight% / O / A / PA / S overflow / 34.7 / 78.0 / 7.6 / 4.7 / 9.8 underflow / 65.3 / 68.4 / 9.8 / 3.9 / 17.9 feed / 100 / na / na / na / 15.1
8/1/82-3	-same as for experiment 8/1/82-1 except that: (a) feed rate 2.2 kg/min (b) pressure drop 1.69 MPa (245 psi) and the feed concentration was 5.0% solids	fraction / weight% / S overflow / 40.6 / 3.1 underflow / 59.4 / 6.3 feed / 100 / 5.0

TABLE 5: FILTRATION TESTS

Experiment Number	Summary of Experimental Procedure and Conditions	Summary of Experimental Results
11/11/82-1	-M4X5 product from exp. 06 run 05 was filtered under vacuum (up to 1 mm HGa) through different filter materials. The filter calc. was not washed. Filtration was carried out at a temperature range of 80-180°C. The effects of filter aids and filter calc. thickness were not investigated. Extensive laboratory scale filtration work has been reported by others.	-a representative set of results of one of the better filtration experiments is:

fraction	weight%	O	A	PA	S
feed	100				10.4
filtrate	N74	73.1		26.5	0.39
filter cake	N26	53.2	3.8	4.8	38.9

SBRG

DISCUSSION

The experimental results are in broad accordance with literature information. Based on these experimental results and information obtained from the literature the performance of each of these unit operations can be summarized as follows:

(a) Settling
   1. depends on or is sensitive to the composition of the materials to be separated
   2. results in 'bottoms' with relatively low solids concentration
   3. results in 'overflows' with relatively high solids content
   4. provides for either no separation or at best only partial separation.

(b) Centrifuge
   1. same as a-1
   2. results in bottoms (centrifuge cake) with relatively high solids concentration
   3. results in overflows with either a relatively high or low solids content depending on the composition of the feed material
   4. provides for either partial separation or near complete separation.

(c) Vacuum evaporation
   1. this method of separation is not sensitive to the composition of the to be separated materials given that most of the liquefaction product can be evaporated without cracking
   2. results in bottoms with a relatively high solids concentration
   3. results in overflows (distillate) which is free of solids
   4. provides for complete separation.

(d) Liquid cyclone
   1. same as a-1
   2. provides for only partial separation and is in essence a pre-thickening device.

(e) Vacuum filtration
   1. same as a-1
   2. may lead to filtration rates which are excessively slow
   3. given that the material can be filtered by vacuum filtration it:
      - results in a bottoms (filter cake) with a relatively high solids concentration
      - results in an overflow (filtrate) with a very low solids content
      - provides for complete separation.

In order to obtain solvent balance in a PDU unit the solids separation must be relatively complete, or in other words the amount of liquid lost with the solids must be small. If this is not the case then very little product will be obtained, and in the extreme it will not be possible to maintain a so called solvent balance. That is, for each cycle less solvent would be available for slurrying the coal. In addition, at least part of the recycle solvent should be relatively free of solids so that the smaller size solid particles do not build-up in the system.

Of the above unit operations the only one which meets these requirements is vacuum evaporation. From the literature it appears that anti-solvent deashing, critical solvent deashing, and pressure filtration with pre-coat also satisfy these requirements. Thus putting full scale factors such as cost and reliability aside for a PDU operation these three plus vacuum evaporation are possibilities for a PDU solids separation system for coal liquefaction slurry.

APPENDIX III

BATCH TEST CONDUCTED ON THE CASCADE REACTOR

APPENDIX III

BATCH TESTS CONDUCTED ON THE CASCADE REACTOR

Introduction

The purpose of the hot-charge autoclave experiments was to obtain data showing the effect of key variables in order to determine the operating conditions on the continuous unit.

The experiments were therefore conducted in the hot-charge autoclave under conditions which would represent those in the continuous unit under steady state.

The hot-charge autoclave batch unit used in these experiments is fully described in Appendix 2 of SBRG report "Investigation to Determine the Feasibility of Using Bitumen as Solvent for Coal Liquefaction", 1980.

Two important modifications were made, however, on the apparatus. The first modification was the addition of a water condenser to cool the hot gases and a receiver to collect the condensate from venting the gasious phase after reaction.

The second modification was the removal of vessel A1 and the installation of a hydraulic cylinder. The advantage of the hydraulic cylinder is the rapid injection of the required amount of slurry into the preheated reactor without carrying any gas along with the slurry during transfer. The modified hot-charge autoclave unit is shown in Figure 1 .

Eight experiments were conducted in the hot-charge autoclave. The first seven experiments were carried out after the first modification was made and the last experiment was carried out with the hydraulic cylinder installed.

The objective of the first four experiments was to investigate the effect of temperature, residence time and solvent to coal ration on the liquefaction of sub-bituminous-C coal using anthracene oil as solvent and hydrogen gas.

Three experiments were carried out to examine the catalytic effect if any of sub-bituminous-C and lignite ashes for the hydrogenation of anthracene oil solvent using hydrogen.

In the last experiment the coking prepensity of the Wilsonville hydrogenated solvent was tested at high temperature (475°C), in order to verify the hypotisis that the occurence of reactor coking in the continuous Run No. 9 was related to the use of Wilsonville solvent at 460°C.

Procedure

The whole system was pressure tested before each experiment. The system was purged with inert gas at 500 psi several times hydrogen was charged into the reactor at a predetermined cold pressure and its volume was measured repeatedly, at the same pressure, using the wet-test meter until successive measurements within one litre were obtained.

For the first seven experiments a weighed amount of slurry was introduced into the vessel A1. Hydrogen was added into A1 to a predetermined cold pressure and its volume was measured, as above, using the wet-test meter.

The reactor was heated to the required temperature. The inside temperature of the reactor was controlled and recorded.

Vessel A1 was heated to 433°K. After the transfer of the slurry from vessel A1 to the reactor, the temperature of the reactor returned to its operating temperature within four minutes.

The volume of hydrogen remained in A1, after transfering was measured by venting through the water condenser and light receiver. By difference the volume of hydrogen transfered along with the slurry into the reactor was obtained.

At the end of the experiment the hot slurry was discharged from the reactor into the liquid receiver and the volume of the reactor gases was measured by venting through the water condenser and light product receiver.

Samples of gases were taken periodically during the experiment and analysed by gas chromatography. The liquid products in both receivers were collected and weighed. When the vessels cooled down the slurry remained in A1 after transfer was recovered using a suitable solvent and subtracted from total slurry. Similarly the weight of liquid remained on the walls of the reactor and liquid receiver was obtained and added to the weight of the liquid product collected.

Experiment seven was conducted with the hydraulic cylinder instead of vessel A1. The slurry was drawn into the cylinder by suction when the piston was moved slowly downwards using the hydraulic jack. The piston was then moved slowly upwards, using the hydraulic jack, until all air was expelled from the cylinder. Inert gas, such as nitrogen, was introduced in the other side of the piston at a predetermined pressure that enabled the rapid injection of slurry into the reactor.

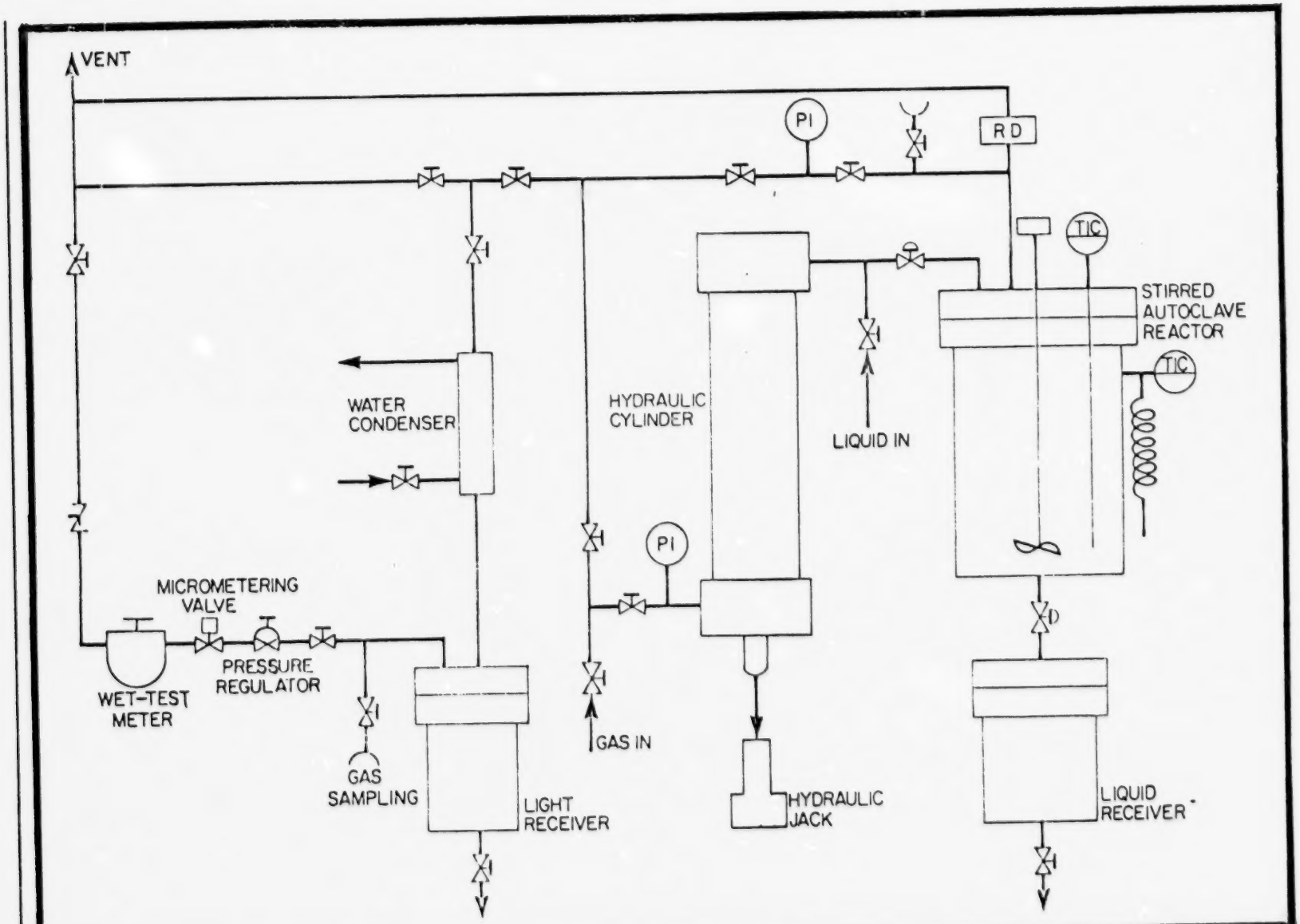


Figure 1 **SBRG Hot Charge Autoclave Batch Unit**

SBRG

TABLE 1 BATCH EXPERIMENTS: REACTION CONDITIONS AND RESULTS[1)]

Exp. No	1	2	3	4
Coal type	Sub-C	Sub-C	Sub-C	Sub-C
Solvent	A.O[2)]	A.O.	A.O.	A.O.
Solvent/coal (Kg/Kg)	2/1	4/1	2/1	2/1
Temperature (°C)	425	425	400	425
Pressure (MPa)	22.8	20.6	20.7	20.7
Retention Time (min)	25	25	25	45
Stirring speed (rpm)	500	500	500	500
% maf coal				
Conversion	69.8	73.0	56.9	76.5
Yields: unconverted	30.2	27.0	43.1	23.5
liquid	66.3	62.5	44.1	73.5
H2O	(5.9)	5.9	6.5	(0.2)
H2 consumed	(3.1)	(6.0)	(2.6)	(1.9)
CO	-	-	0.9	0
CO2	10.6	8.3	7.2	4.3
CH4	0.7	1.4	0.2	0.4
C2H6	0.6	0.9	0.2	0.4
C3H8+	0.6	-	0.1	-

1) all experiments used hydrogen as reducing agent
2) A.O. = anthracene oil

Feedstock

The properties of the solvents, coals and hydrogen gas used in these experiments are shown in Tables 5.5 to 5.7.

The ashes were obtained by ASTM method.

The reactants and the conditions under which the experiments were conducted are shown in Table 5.22.

Results

The results of the experiments are shown in Tables 1 and 2 . The mass balance was calculated by dividing the weight of the total product by the weight of the total feed. The conversion and yields were calculated as described in Section 5.2.

The following observation can be made:

The first four experiments using sub-C, anthracene oil and hydrogen gave the indication that higher temperature, longer residence time and higher solvent /coal ration favour higher conversions. The continuous tests conducted later on confirmed these trends. The range of conversions obtained in the batch testing was improved in the continuous tests, the water and $CO+CO_2$ yields which are an expression of the deoxygenation taking place, were much lower in the batch testing, the same can be said about the gas formation, consequently better gross liquid yields were obtained in the batch mode.

In experiments 5-7 the sub-bituminous and lignite ashes appear to have no catalytic effect on anthracene oil solvent.

Elemental analyses of product removed from the autoclave (Table 2) do not indicate measurable hydrogenation of the solvent at the conditions tested. The result would appear to justify the assumption adopted in liquid calculations (section 5.2 of this report) that the solvent is not changed in the process. There remains though the possibility of a synergistic effect of ash/coal/solvent at the reaction conditions, which even though impossible to quantify, is probably present. The one way of minimizing this effect is an integrated operation where the solvent recirculate in the process and only net products are separated and quantified.

The test No. 8, conducted with Wilsonville at 475°C did not result in coking, suggesting that the occurrence of coke in the reactor was the result of a combination of factors rather than solvent quality alone.

TABLE 2 BATCH EXPERIMENTS: HYDROGENATION OF SOLVENT IN PRESENCE OF COAL ASH*

Exp No.	Ash Type	Product fraction Boiling Range	% wt	Elemental Composition (% wt) C	H	N	S+O	H/C
5	none added	< 205°C	0.4	88.2	8.4	0.5	2.8	1.14
		205-350	56.3	91.0	6.3	0.7	2.0	0.83
		350-407	31.9	92.4	5.6	1.0	1.0	0.73
		407-450	4.9	91.0	5.3	1.2	2.5	0.70
		450+	6.5	90.8	6.21	0.82	2.2	0.82
6	Sub-C	< 205°C	0.4	86.1	7.5	1.0	5.4	1.04
		205-350	57.9	91.2	6.4	0.6	1.8	0.84
		350-407	29.3	92.0	5.7	0.9	1.4	0.74
		407-437	4.3	91.7	5.7	0.7	1.9	0.75
		437+	8.1	90.7	6.1	0.9	2.3	0.81
7	lignite	< 205°C	0.2	90.0	7.0	1.0	2.0	0.93
		205-350	65.0	91.2	6.4	0.7	1.7	0.84
		350-407	23.4	92.7	5.6	1.0	0.5	0.72
		407-450	3.6	90.9	5.3	1.3	0.8	0.70
		450+	7.8	91.7	6.2	0.8	1.3	0.82
Feed	A.O.	< 205°C	3.5	92.0	6.6	0.5	0.9	0.86
		205-350	59.9	91.7	6.1	0.8	1.4	0.80
		350-400	26.6	92.8	5.5	1.2	0.5	0.71
		400-412	4.5	91.6	5.4	1.9	1.1	0.71
		412+	5.5	87.6	4.8	3.2	4.4	0.66

* Experiments were conducted with anthracene oil and hydrogen at the conditions:
temperature = 425°C
pressure = 20.2 MPa
reaction time = 45 min
stirring speed = 700 rpm

POOR

QUALITY

ORIGINAL